Cyclometallated Tantalum Diphenolate Pincer Complexes: Intramolecular C-H/M-CH_3 σ-Bond Metathesis Faster than O-H/M-CH_3 Protonolysis

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Supporting Information

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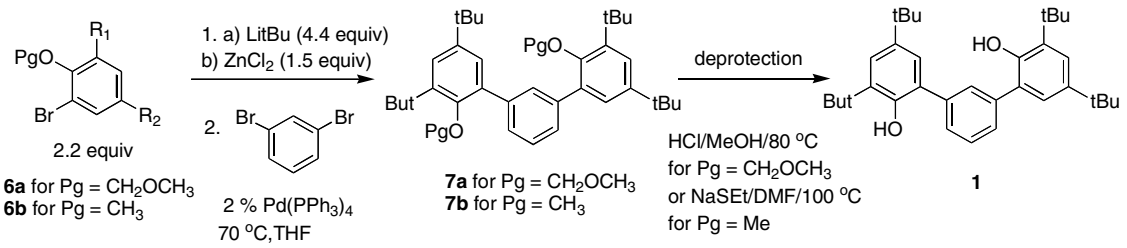
Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or by the method of Grubbs.[1] Benzene-d_6 was purchased from Cambridge Isotopes and distilled from sodium benzophenone ketyl. Chloroform-d_1 and chlorobenzene-d_5 were purchased from Cambridge Isotopes and distilled from calcium hydride. Other materials were used as received. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300, or Varian INOVA-500 spectrometers and unless otherwise indicated at room temperature. Chemical shifts are reported with respect to internal solvent: 7.16 and 128.38 (t) ppm (C_6D_6); 7.27 and 77.23 (t) ppm ($CDCl_3$), for ^{1}H and ^{13}C data; and 5.32 ppm (CH_2Cl_2) for ^{2}H data.



Scheme 1. Synthesis of benzene-1,3-bisphenol (**1**).

Synthesis of (MOMO)BrC$_6$H$_2$-tBu$_2$ (6a). Bromine (3.7 mL, 11.6 g, 72.5 mmol, 1 equiv) was added via syringe to a solution of 2,4-di-t-butyl-phenol (15 g, 72.8 mmol, 1 equiv) in CH_2Cl_2 (200 ml). The brown color of Br_2 disappeared upon addition. GC-MS analysis after 5 min shows only the presence of the desired brominated product (M^+=286). The organic mixture was washed with water, then dried over $MgSO_4$, and filtered. Upon removal of volatile material by rotary evaporation, a golden oil was obtained which solidified after placing under high vacuum (<1 mTorr). This material (4,6-di-t-butyl-2-bromophenol) was dissolved in dry THF (200 mL), under argon, and was deprotonated with NaH (1.92 g, 80 mmol, 1.1 equiv). After the addition of NaH the reaction mixture was stirred for 1 h at room temperature then MOMCl (6.1 mL, 6.5 g, 80.3 mmol, 1.1 equiv) was added via syringe. The reaction mixture was stirred at room temperature for

9 h. Water was added and the mixture was concentrated under vacuum to remove the THF. The desired product was extracted with CH_2Cl_2 (three times). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated to ~50 mL. CaH_2 was added and stirred at room temperature for 6 h then at 100 °C, under vacuum, for 1 h. The reaction vessel was sealed with a needle valve and brought inside an inert atmosphere glove box. The mixture was filtered through a pad of activated alumina with the aid of some Et_2O. Volatiles were removed under vacuum to give 23.5 g (98 % yield over two steps) of desired product **6a**, as a golden oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 3.70 (s, 3H, OCH_3), 5.23 (s, 2H, OCH_2O), 7.32 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz), 7.41 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.0 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 36.1 (*C*(CH$_3$)$_3$), 57.9 (OCH$_3$), 99.5 (OCH$_2$O), 117.7, 124.1, 128.9, 144.6, 147.8, 150.7 (aryl). GC-MS: M^+=328.

Synthesis of (MeO)BrC$_6$H$_2$-tBu$_2$ (6b). A procedure analogous the synthesis of **1a** was employed. The MOMCl was replaced with Me_2SO_4 as alkylating agent. Starting from 20 g of 2,4-di-t-butyl-phenol, 26.8 g (92 % yield over two steps) of **6b** were obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (s, 9H, C(CH_3)$_3$), 1.41 (s, 9H, C(CH_3)$_3$), 3.92 (s, 3H, OCH_3), 7.29 (d, 2H, aryl-*H*, ^{4}J = 2.3 Hz), 7.42 (d, 2H, aryl-*H*, ^{4}J = 2.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.1 (C(*C*H$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 35.9 (*C*(CH$_3$)$_3$), 61.5 (OCH$_3$), 117.8, 123.8, 129.0, 144.2, 147.4, 154.3 (aryl). GC-MS: M^+=298.

Synthesis of (HOC$_6$H$_2$-tBu$_2$)$_2$C$_6$H$_4$ (1). A mixture of **6b** (8.0 g, 26.8 mmol, 1 equiv) and THF (100 mL) in a Schlenk tube fitted with a screw-in Teflon stopper was frozen in a cold well, in an inert atmosphere glove box. This mixture was allowed to thaw and tBuLi solution (1.7 in pentanes, 33 mL, 56.1 mmol, 2.1 equiv) was added via syringe. The mixture was stirred for 1 h, allowing to reach room temperature. $ZnCl_2$ (2.6 g, 20 mmol, 0.7 equiv) was added with the aid of 25 mL THF. After stirring the reaction mixture for 30 minutes, 1,3-dibromobenzene (2.84 g, 12.0 mmol, 0.45 equiv) and $Pd(PPh_3)_4$ (0.31 g, 0.27 mmol, 0.01 equiv) with the aid of some THF (~25 mL). The reaction vessel was placed in an oil bath preheated to 75 °C. Upon stirring for 16 h the mixture was allowed to cool to room temperature and was quenched with water.

Volatile materials were removed under vacuum and water was added (~ 150 mL). This mixture was extracted with Et_2O (three times). The combined organics were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The resulting residue was suspended in MeOH and cooled to -25 °C. The white precipitate was collected by filtration through a sintered glass funnel and washed with cold MeOH. This procedure generates 5.6 g of **7b** as a white powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.35 (s, 18H, C(C*H*$_3$)$_3$), 1.45 (s, 18H, C(C*H*$_3$)$_3$), 3.34 (s, 6H, OC*H*$_3$), 7.22 (d, 2H, aryl-*H*, ^{4}J = 2.5 Hz), 7.36 (d, 2H, aryl-*H*, ^{4}J = 2.5 Hz), 7.45-7.51 (m, 1H, 5-C$_6$H$_3$-*H*), 7.56 (app dt, 2H, 4,6-C$_6$H$_2$-*H*$_2$), 7.81 (app t, 1H, 2-C$_6$H$_3$-*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.2 (C(*C*H$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 34.8 (*C*(CH$_3$)$_3$), 35.6 (*C*(CH$_3$)$_3$), 60.4 (OCH$_3$), 123.6, 126.9, 127.8, 128.6, 130.0, 134.6, 140.9, 142.2, 145.6, 155.2 (aryl). GC-MS: M^+=514. Compound **7b** (5.6 g, 10.9 mmol, 1 equiv) obtained above was suspended in DMF (60 mL).[2] NaSEt was prepared in situ by the slow addition of EtSH (3.2 mL, 2.7 g, 43.3 mmol, 4 equiv) and NaH (1.04 g, 43.3 mmol, 4 equiv). The resulting mixture was heated to 110 °C for 5 hours, then cooled and an aliquot was collected and inspected by GC-MS to show the formation of the free phenol (M^+=486). Water (60 mL) was added and the resulting mixture was extracted with Et_2O, dried over $MgSO_4$, and filtered. Volatile materials were removed by rotary evaporation with mild heating. The residue was triturated with MeOH a couple of times, then suspended in MeOH (20 mL) and cooled to -25 °C. A white precipitate was collected by filtration and washed with cold MeOH. The collected solid was placed under vacuum to give 4.77 g (9.8 mmol, 81 % yield over two steps) desired product **1**.

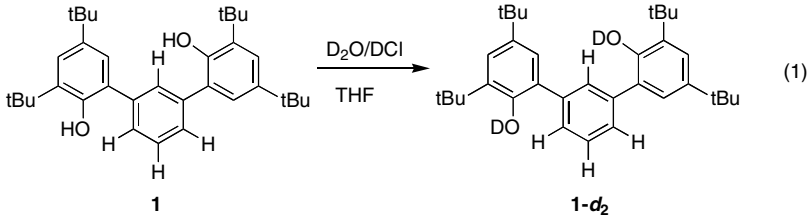
Preparation of **1** using **6a** as starting material involves an analogous palladium coupling to give the terphenyl framework **7a**. This material was carried over to the step involving removal of protecting group. Compound **7a** was suspended in MeOH and concentrated HCl was added. This mixture was heated at 80 °C for 2-6 h. Upon cooling down, volatile materials were removed under vacuum and the desired product (**3**) was obtained as above. Starting from 1.24 g of 1,3-dibrombenzene led to the isolation of 1.83 g (72 % yield) of **1**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.36 (s, 18H, C(C*H*$_3$)$_3$), 1.49 (s, 18H, C(C*H*$_3$)$_3$), 5.51 (s, 2H, O*H*), 7.15 (d, 2H, aryl-*H*, ^{4}J = 2.5 Hz), 7.39 (d, 2H, aryl-*H*, ^{4}J = 2.5

Hz), 7.55 (app dt, 1H, 2H, 4,6-C_6H_2-H_2), 7.61-7.66 (m, 2H, 2,5-C_6H_2-H_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.0 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 124.3, 125.0, 127.8, 129.0, 130.4, 131.1, 135.9, 139.5, 142.5, 148.9 (aryl).

Preparation of $Ta(CH_3)_2[(OC_6H_2$-$tBu_2)_2C_6H_3]$ (3). KBn (234 mg, 1.8 mmol, 2 equiv) was added as a solid to an Et_2O / THF (17 / 1 mL respectively) solution of diphenol **1** (437 mg, 0.90 mmol, 1 equiv). Orange solid KBn dissolves and discolors over less than an hour. The reaction mixture was allowed to react for 2 h, then $TaCl_2Me_3$ (267 mg, 0.90 mmol, 1 equiv) was added. Within minutes, the color of the reaction mixture turns brown. The mixture was stirred for 4 hours then filtered through a bed of Celite. Volatile materials were removed under vacuum. Petroleum ether was added to the brown residue and the mixture was stirred for ~ 10 minutes. This mixture was filtered through Celite to remove dark solids. The pale brown filtrate was concentrated and cooled to -35 °C. The resulting white precipitate was collected by filtration, washed with cold petroleum ether, and dried under vacuum. This procedure affords 339 mg (0.49 mmol, 54 % yield) of **3** as a white powder. ^{1}H NMR (500 MHz, C_6D_6) δ: 0.81 (s, 6H, $Ta(CH_3)_2$), 1.40 (s, 18H, $C(CH_3)_3$), 1.73 (s, 18H, $C(CH_3)_3$), 7.48 (t, 1H, C_6H_2-H, ^{3}J = 8 Hz), 7.69 (d, 2H, aryl-H, ^{4}J = 2.4 Hz), 8.04 (d, 2H, aryl-H, ^{4}J = 2.4 Hz), 8.23 (d, 2H, C_6H-H_2, ^{3}J = 8 Hz). ^{13}C NMR (125 MHz, C_6D_6) δ: 31.3 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 35.3 ($C(CH_3)_3$), 35.8 ($C(CH_3)_3$), 60.6 ($TaCH_3$), 123.8, 125.1, 131.2, 135.4, 137.4, 144.1, 144.8, 153.6 (aryl), 198.5 (aryl-CTa). Anal. calcd. for $C_{36}H_{49}O_2Ta$ (%): C, 62.24; H, 7.11. Found: C, 60.88; H, 7.24.

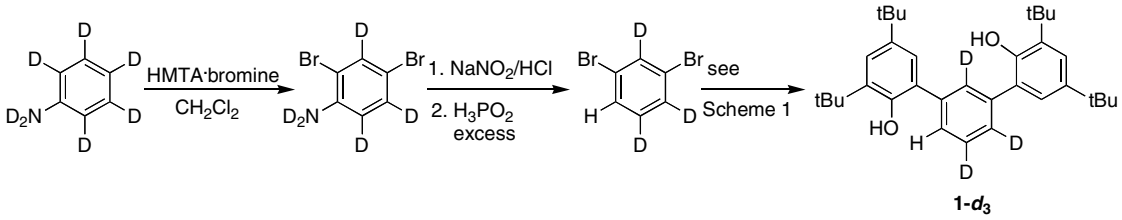
Preparation of $TaCl_2(CH_3)[(OC_6H_2$-$tBu_2)_2C_6H_4]$ (4). An Et_2O (5 mL) solution of biphenol **3** (152 mg, 0.31 mmol, 1 equiv) was added to an Et_2O (5 mL) solution of $TaCl_2(CH_3)_3$. The reaction mixture changes gradually from colorless to yellow. The mixture was stirred for 16 h, then volatile materials were removed under vacuum. The residue was suspended in petroleum ether and cooled to -35 °C. A yellow precipitate was collected by filtration and washed with cold petroleum ether. Drying under vacuum gives 131 mg (0.17 mmol, 56 % yield) of 4 as a bright yellow powder. ^{1}H NMR (300 MHz, C_6D_6) δ: 1.31 (s, 18H, $C(CH_3)_3$), 1.74 (s, 18H, $C(CH_3)_3$), 2.27 (s, 3H, $TaCH_3$), 7.02 (dd, 2H, C_6H_2-H_2, ^{4}J = 1.8 Hz, ^{3}J = 7.8 Hz), 7.17 (t, overlap with C_6D_5H, 1H, C_6H_3-H, ^{3}J = 7.8 Hz), 7.38 (d, 2H,

aryl-*H*, ^{4}J = 2.4 Hz), 7.52 (t, 1H, C_6H_3-*H*, ^{4}J = 1.8 Hz), 7.69 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2) δ: 31.2 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 36.0 ($C(CH_3)_3$), 69.3 ($TaCH_3$), 112.6, 124.7, 125.0, 130.9, 133.4, 134.9, 138.4, 145.3, 147.7, 157.5 (aryl). Anal. calcd. for $C_{35}H_{47}Cl_2O_2Ta$ (%): C, 55.93; H, 6.30. Found: C, 54.81; H, 6.06.



(1)

Synthesis of $(DOC_6H_2\text{-}tBu_2)_2C_6H_3$ (1-*d*$_2$, eq 1). A dry THF (10 mL) solution of compound **3** (200 mg) was placed in a flask previously flame dried and rinsed with D_2O. D_2O was added until precipitation was observed. Volatile materials were removed by rotary evaporation. Dry THF (10 mL) was added, followed by precipitation with D_2O. This procedure was repeated three times. The OH peaks are absent by ^{1}H NMR spectroscopy.



Scheme 2. Preparation of labeled diphenol **1-*d*$_3$**.

Synthesis of $(HOC_6H_2\text{-}tBu_2)_2C_6HD_3$ (1-*d*$_3$). 2,4-Dibromoaniline-d_5 was prepared according to the literature procedure for the non-deuterated version, starting from aniline-d_7 (0.30 g, 3.0 mmol).[3] Resulting 2,4-Dibromoaniline-d_5 was all submitted to the following step, by mixing with water, adding concentrated HCl (2 mL), and cooling in a ice / water bath. $NaNO_2$ (0.23 g, 3.3 mmol, 1.1 equiv) was added to the resulting cold mixture and the mixture was stirred for 1 h at 0 °C.[4] H_3PO_2 was added (6 g 50 % solution, 45 mmol, 15 equiv) and the reaction mixture was allowed to warm up to room temperature and was stirred for 3 hours. This solution was extracted with CH_2Cl_2. The organic fraction was dried over $MgSO_4$ and filtered. Volatile materials were removed by

rotary evaporation to generate $C_6Br_2D_3H$ as a colorless oil (0.1845 g, 0.77 mmol, 25 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (s, $C_6Br_2D_3H$). GC-MS: M^+=239. This material was used as precursor for the synthesis of **1-*d*$_3$** by using the procedure above with **1a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.34 (s, 18H, $C(CH_3)_3$), 1.47 (s, 18H, $C(CH_3)_3$), 5.37 (s, 2H, O*H*), 7.13 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz), 7.38 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz), 7.53 (s, 1H, 2H, 4-C_6D_3-*H*).

Reaction of 1-*d*$_3$ with $TaCl_2(CH_3)_3$. A solution of $TaCl_2(CH_3)_3$ (7.3 mg, 0.025 mmol, 1 equiv) in C_6D_6 (0.4 mL) was placed in a J-Young tube and a solution of **1-*d*$_3$** (12.1 mg, 0.025 mmol, 1 equiv) in C_6D_6 (0.4 mL) was added with the aid of C_6D_6 (~ 0.3 mL). The NMR tube was sealed and mechanically rotated for 10 hours after which the reaction mixture was investigated by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6) aromatic region, δ: 7.02 (d, 1H, C_6D_2H-*H*, ^{4}J = 1.7 Hz), 7.38 (two d, 2H, aryl-*H*, ^{4}J = 2.4 Hz), 7.51 (d, 0.76H, C_6D_2H-*H*, ^{4}J = 1.7 Hz), 7.69 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz). Methane region, δ: 0.14 (t, 0.29H, CDH_3), 0.16 (s, 0.71H, CH_4). ^{2}H NMR (75 MHz, CH_2Cl_2, recorded upon product isolation): δ: 7.40, 7.80 (br s).

Reaction of 1-*d*$_2$ with $TaCl_2(CH_3)_3$. A solution of $TaCl_2(CH_3)_3$ (7.2 mg, 0.024 mmol, 1 equiv) in C_6D_6 (0.4 mL) was placed in a J-Young tube and a solution of **1-*d*$_2$** (11.9 mg, 0.024 mmol, 1 equiv) in C_6D_6 (0.4 mL) was added with the aid of C_6D_6 (~ 0.3 mL). The NMR tube was sealed and mechanically rotated for 10 hours after which the reaction mixture was investigated by NMR spectroscopy. ^{1}H NMR (500 MHz, C_6D_6) aromatic region, δ: 7.02 (d, 2H, C_6HD-H_2, ^{3}J = 7.6 Hz), 7.17 (t, overlap with C_6D_5H, 1H, C_6DH_2-*H*, ^{3}J = 7.6 Hz), 7.38 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz), 7.51 (t, 0.16H, C_6H_3-*H*), 7.69 (d, 2H, aryl-*H*, ^{4}J = 2.4 Hz). Methane region, δ: 0.14 (t, 0.59H, CDH_3), 0.16 (s, 0.71H, CH_4). ^{2}H NMR (75 MHz, CH_2Cl_2, recorded upon product isolation): δ: 7.13 (br s).

Preparation of 5. A C_6D_6 (0.6 mL) solution of **4** (15 mg) was placed in a J-Young tube, sealed, and immersed almost completely in an oil bath at 110 ºC, behind a blast shield. After 10 h, the sample was cooled to room temperature. ^{1}H and ^{13}C spectroscopic analysis show the clean formation of the species assigned to **5**. ^{1}H NMR (500 MHz, C_6D_6)

δ: 1.35 (s, 18H, C(CH_3)$_3$), 1.74 (s, 18H, C(CH_3)$_3$), 7.31 (t, 1H, C_6H_2-*H*, ^{3}J = 7.8 Hz), 7.66 (d, 2H, aryl-*H*, ^{4}J = 2 Hz), 7.85 (d, 2H, aryl-*H*, ^{4}J = 2 Hz), 8.04 (d, 2H, C_6H-H_2, ^{3}J = 7.8 Hz). ^{13}C NMR (125 MHz, C_6D_6) δ: 31.4 (C(*C*H$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 35.3 (*C*(CH$_3$)$_3$), 35.9 (*C*(CH$_3$)$_3$), 124.4, 124.5, 128.3, 133.9, 135.2, 138.2, 144.2, 146.5, 154.0 (aryl), 205.4 (aryl-*C*Ta).

Kinetic measurements for the conversion of 4 to 5. Stock solutions containing **4** and Ph_2CH_2 as a standard were prepared in C_6D_5Br and stored at -35 ºC. The NMR probe was brought to the desired temperature and calibrated with an ethylene glycol standard. After the NMR run was complete, the temperature was checked again. Deflections less than a degree were found indicating temperature stability during experiment. A J-Young tube charged with the solution of **4** was utilized in these experiments. The decay of the Ta-CH_3 peak was integrated against the methylene hydrogens of the standard Ph_2CH_2. Data was acquired for at least three half lives. The data was plotted using Microsoft Excel. The standard error for each rate constant measurement was found to be less than 1 % using the regression function in Excel.

X-ray Crystal Data: General Procedure. Crystals grown from benzene (**7** and **8**) or a mixture of diethyl ether and petroleum ether (**13**) at -35 °C were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker Smart 1000 CCD diffractometer. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Some details regarding refined data and cell parameters are available in Table 1. Selected bond distances and angles are supplied in the captions of Figures 2, 4, and 7.

Table 1. Crystal and Refinement data for complexes **4** and **5-OEt$_2$**.

	4	**5-OEt$_2$**
Empirical formula	$2(C_{35}H_{47}O_2Cl_2Ta) \bullet C_6H_6$	$C_{38}H_{53}O_3Cl_2Ta$
Formula weight	1581.26	809.65
T (K)	100(2)	100(2)

a, Å	11.2683(7)	15.0003(3)
b, Å	17.5151(11)	15.1231(3)
c, Å	18.2677(12)	16.5600(4)
α, deg	88.7480(10)	95.7320(10)°
β, deg	88.5720(10)	97.0480(10)
γ, deg	89.2020(10)	91.9980(10)°
Volume, Å^3	3603.1(4)	3705.40(14)
Z	2	4
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
d_{calc}, g/cm^3	1.457	1.451
θ range, deg	1.59 to 33.65	1.35 to 50.18
μ, mm^{-1}	3.229	3.144
Abs. Correction	None	None
GOF	1.622	1.000
R_1,[a] wR_2[b] [I>2σ(I)]	0.0605, 0.1014	0.0390, 0.0748

[a] $R_1 = \bullet | |F_o| - |F_c| | / \bullet |F_o|$. [b] $wR_2 = [\bullet[w(F_o^2-F_c^2)^2] / \bullet[w(F_o^2)^2]]^{1/2}$.

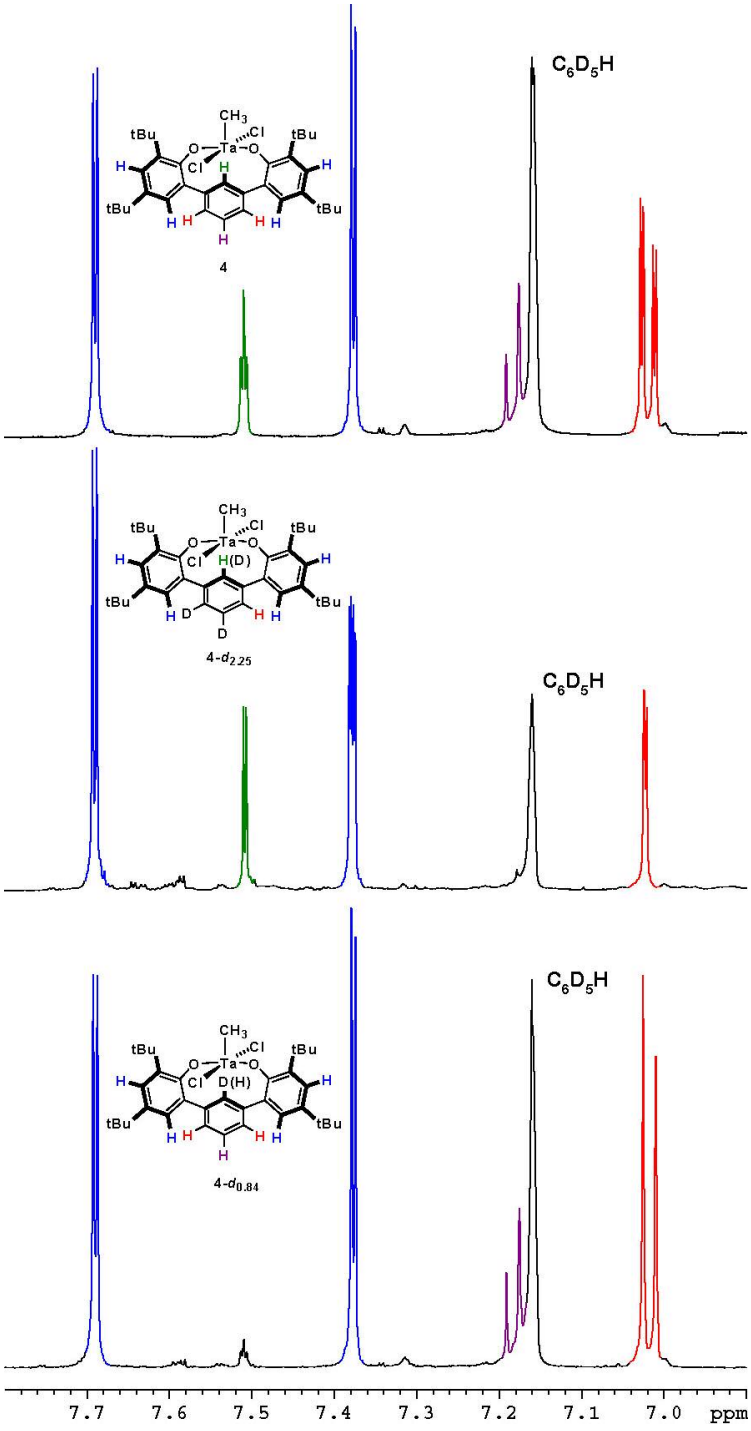


Figure 1. Aromatic reagion of the ^{1}H NMR spectra (C_6D_6) of different isotopologs of **4**.

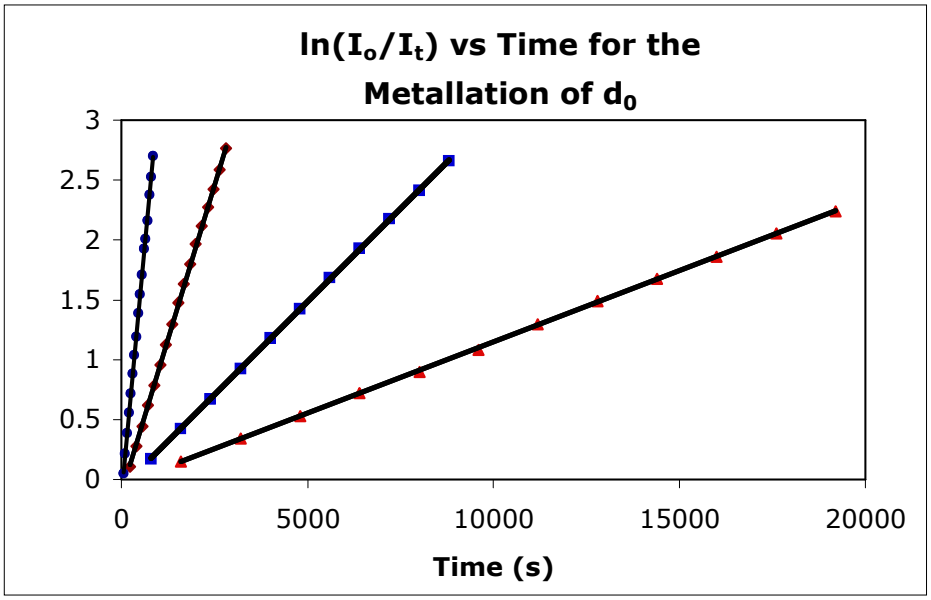


Figure 2. Kinetic plots for the cyclometallation of **4** at different temperatures (91 °C – red triangles, 101 °C – blue squares, 111 °C – red diamonds, 125 °C – blue circles).

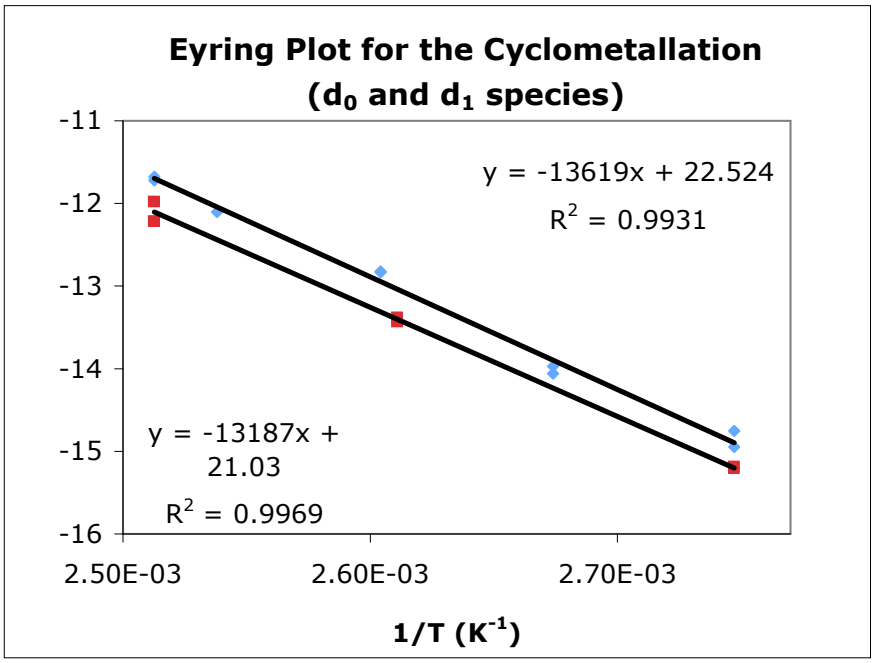


Figure 3. Eyring plots for the cyclometallation of **4** (blue) and **4-*d*$_1$** (red).

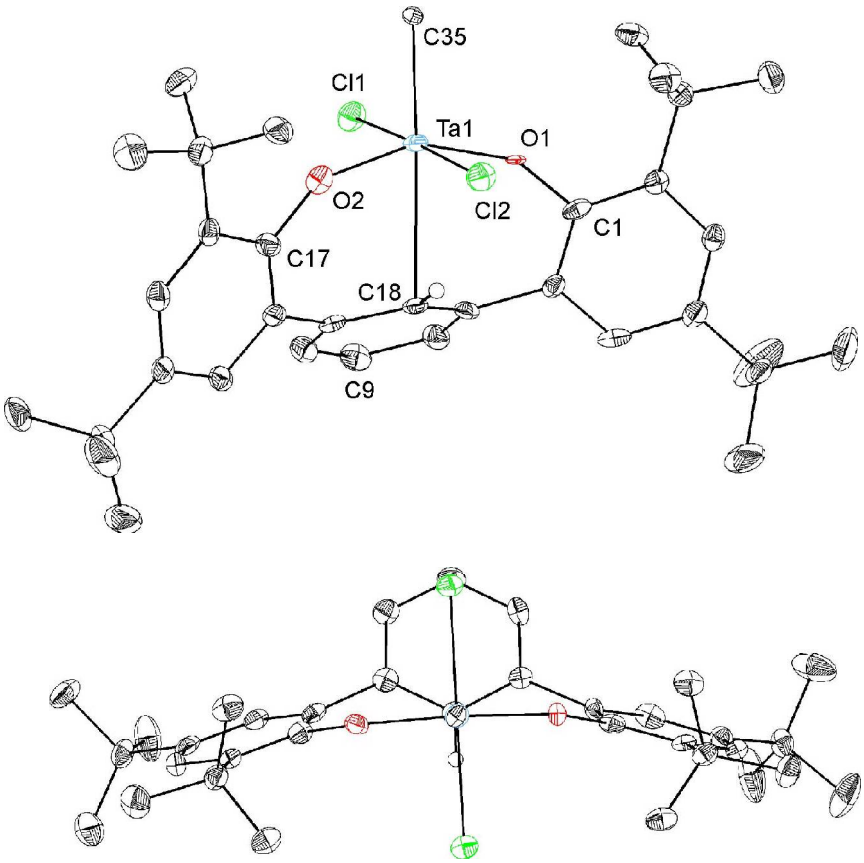


Figure 4. Structural drawing of **4** with displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ta-O1 1.876(4); Ta-O2 1.859(4); Ta-C35 2.147(4); Ta-C18 2.7913(47); Ta-C18-C9 ; O1-Ta-O2 152.45(15); Ta-O1-C1 151.7(3); Ta-O2-C17 149.1(4).

Special Refinement Details

Visual inspection of the diffraction images show the crystal is an obvious twin. The two components of the twin are related by an approximate 2-fold around the *a*-axis (*a** in reciprocal space) and orientation matrices for each component were calculated using CELL_NOW. However, attempts to integrate intensities separately for each to incorporated in least-squares refinement as a twinned crystal were unsuccessful. The four molecules in the unit cell have coordinates that are related to each with approximate $P2_1/c$ symmetry. The Laue symmetry of the diffraction pattern does not reflect 2/m symmetry as would be required by $P2_1/c$. Additionally, O(1) in each molecule refined as non-positive

definite so a restraint was imposed on these oxygens causing the anisotropic displacement parameters to approximate isotropic behavior.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 4 (CCDC 626578). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ta(1)	8977(1)	4766(1)	1808(1)	15(1)
Cl(1A)	10547(1)	4743(1)	2633(1)	22(1)
Cl(2A)	7323(1)	4795(1)	1024(1)	22(1)
O(1A)	8700(3)	5812(2)	1943(2)	11(1)
O(2A)	8661(3)	3741(2)	2002(2)	19(1)
C(1A)	8046(4)	6406(3)	2221(3)	17(1)
C(2A)	8026(4)	7121(3)	1875(3)	15(1)
C(3A)	7348(4)	7691(3)	2217(3)	17(1)
C(4A)	6718(4)	7580(3)	2868(3)	19(1)
C(5A)	6793(4)	6866(3)	3209(3)	21(1)
C(6A)	7444(4)	6263(3)	2893(3)	15(1)
C(7A)	7614(4)	5531(3)	3310(3)	14(1)
C(8A)	8022(5)	5552(3)	4016(3)	20(1)

C(9A)	8234(5)	4887(3)	4413(3)	22(1)
C(10A)	8069(5)	4189(4)	4100(3)	21(1)
C(11A)	7640(4)	4137(3)	3389(3)	17(1)
C(12A)	7487(4)	3372(3)	3069(3)	16(1)
C(13A)	6876(4)	2803(3)	3466(3)	18(1)
C(14A)	6784(4)	2077(3)	3202(3)	19(1)
C(15A)	7337(5)	1915(3)	2530(3)	20(1)
C(16A)	7971(5)	2447(3)	2103(3)	18(1)
C(17A)	8014(4)	3187(3)	2397(3)	18(1)
C(18A)	7395(4)	4825(3)	3006(3)	15(1)
C(19A)	8747(5)	7291(3)	1162(3)	19(1)
C(20A)	8309(5)	6800(4)	539(3)	26(1)
C(21A)	8636(6)	8133(3)	914(3)	29(1)
C(22A)	10063(5)	7125(4)	1292(3)	24(1)
C(23A)	6024(5)	8233(3)	3237(3)	22(1)
C(24A)	5643(7)	8849(4)	2672(4)	49(2)
C(25A)	6824(6)	8600(5)	3768(4)	53(2)
C(26A)	4893(6)	7947(4)	3605(5)	52(2)
C(27A)	6120(5)	1439(3)	3627(3)	23(1)
C(28A)	5450(6)	1748(4)	4320(4)	42(2)
C(29A)	7036(5)	857(4)	3921(4)	33(2)
C(30A)	5237(6)	1064(4)	3164(4)	41(2)
C(31A)	8595(5)	2246(3)	1382(3)	21(1)
C(32A)	8446(6)	1404(4)	1200(3)	33(2)
C(33A)	8099(5)	2723(4)	742(3)	25(1)
C(34A)	9950(5)	2371(4)	1432(3)	27(1)
C(35A)	10218(4)	4697(3)	899(3)	12(1)
Ta(2)	992(1)	9705(1)	3195(1)	15(1)
Cl(1B)	-594(1)	9731(1)	2385(1)	24(1)
Cl(2B)	2655(1)	9678(1)	3969(1)	22(1)
O(1B)	1293(3)	10744(2)	3034(2)	12(1)
O(2B)	1298(3)	8685(2)	3007(2)	18(1)
C(1B)	1945(4)	11316(3)	2723(3)	17(1)
C(2B)	1989(4)	12028(3)	3048(3)	17(1)
C(3B)	2650(4)	12589(3)	2673(3)	21(1)

C(4B)	3244(4)	12468(3)	2001(3)	19(1)
C(5B)	3146(4)	11756(3)	1696(3)	19(1)
C(6B)	2502(4)	11170(3)	2043(3)	15(1)
C(7B)	2332(4)	10448(3)	1665(3)	17(1)
C(8B)	1907(5)	10469(3)	951(3)	20(1)
C(9B)	1706(5)	9809(3)	585(3)	25(1)
C(10B)	1907(5)	9101(4)	922(3)	22(1)
C(11B)	2330(4)	9051(3)	1628(3)	18(1)
C(12B)	2482(4)	8296(3)	1982(3)	16(1)
C(13B)	3108(4)	7703(3)	1624(3)	18(1)
C(14B)	3197(4)	6973(3)	1915(3)	17(1)
C(15B)	2579(5)	6821(3)	2568(3)	19(1)
C(16B)	1940(5)	7368(3)	2957(3)	18(1)
C(17B)	1934(4)	8108(3)	2665(3)	16(1)
C(18B)	2567(4)	9730(3)	1985(3)	14(1)
C(19B)	1318(5)	12207(4)	3776(3)	20(1)
C(20B)	1761(5)	11687(4)	4394(3)	24(1)
C(21B)	1496(6)	13037(4)	4006(3)	32(2)
C(22B)	-24(5)	12105(4)	3678(3)	27(1)
C(23B)	3931(5)	13120(3)	1629(3)	24(1)
C(24B)	4736(6)	13492(4)	2140(4)	49(2)
C(25B)	3032(5)	13719(4)	1332(3)	29(2)
C(26B)	4648(6)	12841(4)	949(4)	50(2)
C(27B)	3880(5)	6343(3)	1502(3)	24(1)
C(28B)	4962(7)	6656(4)	1117(6)	80(4)
C(29B)	3070(6)	5994(4)	974(4)	47(2)
C(30B)	4299(7)	5709(4)	2036(4)	53(2)
C(31B)	1265(5)	7171(3)	3682(3)	19(1)
C(32B)	1335(6)	6323(4)	3873(3)	31(2)
C(33B)	-63(5)	7388(4)	3624(3)	26(1)
C(34B)	1816(5)	7596(4)	4318(3)	24(1)
C(35B)	-241(4)	9647(3)	4116(3)	12(1)
C(1C)	4742(8)	5384(8)	4368(6)	77(4)
C(2C)	4799(8)	4600(9)	4385(6)	84(4)
C(3C)	5055(7)	4222(7)	5024(7)	76(3)

C(1D)	4794(7)	9267(6)	-146(7)	70(3)
C(2D)	5113(7)	9464(7)	543(6)	66(3)
C(3D)	5302(7)	10203(8)	678(5)	66(3)

Table 3. Selected bond lengths [Å] and angles [°] for 4 (CCDC 626578).

Ta(1)-O(1A)	1.876(4)	O(1A)-Ta(1)-O(2A)	152.45(15)
Ta(1)-O(2A)	1.859(4)	O(1A)-Ta(1)-C(35A)	105.54(17)
Ta(1)-C(35A)	2.147(4)	O(2A)-Ta(1)-C(35A)	101.73(18)
Ta(1)-Cl(1A)	2.3511(14)	O(1A)-Ta(1)-Cl(1A)	91.92(11)
Ta(1)-Cl(2A)	2.3782(14)	O(2A)-Ta(1)-Cl(1A)	91.62(12)
		C(35A)-Ta(1)-Cl(1A)	90.57(14)
		O(1A)-Ta(1)-Cl(2A)	87.22(11)
		O(2A)-Ta(1)-Cl(2A)	87.90(12)
		C(35A)-Ta(1)-Cl(2A)	92.28(14)
		Cl(1A)-Ta(1)-Cl(2A)	177.14(5)
H18(A)-Cl(2A)	2.77		
Ta(2)-O(2B)	1.852(4)	O(2B)-Ta(2)-O(1B)	151.26(15)
Ta(2)-O(1B)	1.870(3)	O(2B)-Ta(2)-C(35B)	102.75(17)
Ta(2)-C(35B)	2.156(4)	O(1B)-Ta(2)-C(35B)	105.73(17)
Ta(2)-Cl(1B)	2.3471(14)	O(2B)-Ta(2)-Cl(1B)	91.09(12)
Ta(2)-Cl(2B)	2.3755(14)	O(1B)-Ta(2)-Cl(1B)	92.53(11)
		C(35B)-Ta(2)-Cl(1B)	90.34(14)
		O(2B)-Ta(2)-Cl(2B)	88.18(12)
		O(1B)-Ta(2)-Cl(2B)	86.96(11)
		C(35B)-Ta(2)-Cl(2B)	92.20(14)
		Cl(1B)-Ta(2)-Cl(2B)	177.46(5)
H18(B)-Cl(2B)	2.77		

Table 4. Bond lengths [Å] and angles [°] for 4 (CCDC 626578).

Ta(1)-O(1A)	1.876(4)	C(23A)-C(26A)	1.512(8)
Ta(1)-O(2A)	1.859(4)	C(23A)-C(24A)	1.541(9)
Ta(1)-C(35A)	2.147(4)	C(23A)-C(25A)	1.501(8)
Ta(1)-Cl(1A)	2.3511(14)	C(27A)-C(30A)	1.490(8)
Ta(1)-Cl(2A)	2.3782(14)	C(27A)-C(29A)	1.540(8)
O(1A)-C(1A)	1.365(6)	C(27A)-C(28A)	1.561(8)
O(2A)-C(17A)	1.400(6)	C(31A)-C(33A)	1.534(8)
C(1A)-C(2A)	1.392(8)	C(31A)-C(32A)	1.531(8)
C(1A)-C(6A)	1.407(7)	C(31A)-C(34A)	1.550(8)
C(2A)-C(3A)	1.397(8)	Ta(2)-O(2B)	1.852(4)
C(2A)-C(19A)	1.544(7)	Ta(2)-O(1B)	1.870(3)
C(3A)-C(4A)	1.381(7)	Ta(2)-C(35B)	2.156(4)
C(4A)-C(5A)	1.389(8)	Ta(2)-Cl(1B)	2.3471(14)
C(4A)-C(23A)	1.536(8)	Ta(2)-Cl(2B)	2.3755(14)
C(5A)-C(6A)	1.404(8)	O(1B)-C(1B)	1.359(6)
C(6A)-C(7A)	1.490(8)	O(2B)-C(17B)	1.383(7)
C(7A)-C(8A)	1.380(7)	C(1B)-C(6B)	1.404(7)
C(7A)-C(18A)	1.394(8)	C(1B)-C(2B)	1.395(8)
C(8A)-C(9A)	1.380(8)	C(2B)-C(3B)	1.398(7)
C(9A)-C(10A)	1.379(8)	C(2B)-C(19B)	1.549(7)
C(10A)-C(11A)	1.403(8)	C(3B)-C(4B)	1.403(8)
C(11A)-C(18A)	1.406(8)	C(4B)-C(5B)	1.384(8)
C(11A)-C(12A)	1.487(8)	C(4B)-C(23B)	1.526(7)
C(12A)-C(17A)	1.393(7)	C(5B)-C(6B)	1.398(7)
C(12A)-C(13A)	1.398(7)	C(6B)-C(7B)	1.470(8)
C(13A)-C(14A)	1.376(8)	C(7B)-C(8B)	1.399(8)
C(14A)-C(15A)	1.396(8)	C(7B)-C(18B)	1.400(8)
C(14A)-C(27A)	1.539(7)	C(8B)-C(9B)	1.373(8)
C(15A)-C(16A)	1.396(7)	C(9B)-C(10B)	1.391(8)
C(16A)-C(17A)	1.415(8)	C(10B)-C(11B)	1.386(8)
C(16A)-C(31A)	1.523(8)	C(11B)-C(18B)	1.402(8)
C(19A)-C(20A)	1.537(8)	C(11B)-C(12B)	1.469(8)
C(19A)-C(22A)	1.530(7)	C(12B)-C(13B)	1.410(8)
C(19A)-C(21A)	1.538(8)	C(12B)-C(17B)	1.414(7)

C(13B)-C(14B)	1.378(8)	Cl(1A)-Ta(1)-Cl(2A)	177.14(5)
C(14B)-C(15B)	1.388(7)	C(1A)-O(1A)-Ta(1)	151.7(3)
C(14B)-C(27B)	1.537(8)	C(17A)-O(2A)-Ta(1)	149.1(4)
C(15B)-C(16B)	1.389(8)	O(1A)-C(1A)-C(2A)	121.6(5)
C(16B)-C(17B)	1.390(8)	O(1A)-C(1A)-C(6A)	116.3(5)
C(16B)-C(31B)	1.545(7)	C(2A)-C(1A)-C(6A)	122.0(5)
C(19B)-C(20B)	1.525(8)	C(1A)-C(2A)-C(3A)	116.8(5)
C(19B)-C(21B)	1.539(8)	C(1A)-C(2A)-C(19A)	122.0(5)
C(19B)-C(22B)	1.540(7)	C(3A)-C(2A)-C(19A)	121.2(5)
C(23B)-C(24B)	1.485(9)	C(4A)-C(3A)-C(2A)	123.8(5)
C(23B)-C(26B)	1.550(9)	C(3A)-C(4A)-C(5A)	117.8(5)
C(23B)-C(25B)	1.547(8)	C(3A)-C(4A)-C(23A)	121.8(5)
C(27B)-C(28B)	1.497(8)	C(5A)-C(4A)-C(23A)	120.3(5)
C(27B)-C(29B)	1.490(8)	C(4A)-C(5A)-C(6A)	121.6(5)
C(27B)-C(30B)	1.539(9)	C(5A)-C(6A)-C(1A)	118.0(5)
C(31B)-C(32B)	1.521(8)	C(5A)-C(6A)-C(7A)	120.1(5)
C(31B)-C(34B)	1.542(7)	C(1A)-C(6A)-C(7A)	121.4(5)
C(31B)-C(33B)	1.544(8)	C(8A)-C(7A)-C(18A)	119.0(5)
C(1C)-C(3C)#1	1.345(14)	C(8A)-C(7A)-C(6A)	118.9(5)
C(1C)-C(2C)	1.373(14)	C(18A)-C(7A)-C(6A)	122.1(5)
C(2C)-C(3C)	1.365(14)	C(7A)-C(8A)-C(9A)	120.9(5)
C(3C)-C(1C)#1	1.345(14)	C(10A)-C(9A)-C(8A)	120.1(6)
C(1D)-C(2D)	1.370(13)	C(9A)-C(10A)-C(11A)	121.2(6)
C(1D)-C(3D)#2	1.334(13)	C(10A)-C(11A)-C(18A)	117.5(5)
C(2D)-C(3D)	1.343(13)	C(10A)-C(11A)-C(12A)	119.4(5)
C(3D)-C(1D)#2	1.334(13)	C(18A)-C(11A)-C(12A)	123.1(5)
		C(17A)-C(12A)-C(13A)	118.4(5)
O(1A)-Ta(1)-O(2A)	152.45(15)	C(17A)-C(12A)-C(11A)	121.3(5)
O(1A)-Ta(1)-C(35A)	105.54(17)	C(13A)-C(12A)-C(11A)	120.2(5)
O(2A)-Ta(1)-C(35A)	101.73(18)	C(14A)-C(13A)-C(12A)	121.3(5)
O(1A)-Ta(1)-Cl(1A)	91.92(11)	C(13A)-C(14A)-C(15A)	118.3(5)
O(2A)-Ta(1)-Cl(1A)	91.62(12)	C(13A)-C(14A)-C(27A)	122.5(5)
C(35A)-Ta(1)-Cl(1A)	90.57(14)	C(15A)-C(14A)-C(27A)	119.2(5)
O(1A)-Ta(1)-Cl(2A)	87.22(11)	C(16A)-C(15A)-C(14A)	124.0(5)
O(2A)-Ta(1)-Cl(2A)	87.90(12)	C(15A)-C(16A)-C(17A)	115.0(5)
C(35A)-Ta(1)-Cl(2A)	92.28(14)	C(15A)-C(16A)-C(31A)	122.7(5)

C(17A)-C(16A)-C(31A)	122.3(5)	O(1B)-Ta(2)-Cl(2B)	86.96(11)
O(2A)-C(17A)-C(12A)	119.3(5)	C(35B)-Ta(2)-Cl(2B)	92.20(14)
O(2A)-C(17A)-C(16A)	117.6(5)	Cl(1B)-Ta(2)-Cl(2B)	177.46(5)
C(12A)-C(17A)-C(16A)	123.0(5)	C(1B)-O(1B)-Ta(2)	151.1(3)
C(7A)-C(18A)-C(11A)	121.3(5)	C(17B)-O(2B)-Ta(2)	152.3(3)
C(20A)-C(19A)-C(22A)	110.2(5)	O(1B)-C(1B)-C(6B)	116.8(5)
C(20A)-C(19A)-C(2A)	110.3(4)	O(1B)-C(1B)-C(2B)	120.8(5)
C(22A)-C(19A)-C(2A)	109.2(4)	C(6B)-C(1B)-C(2B)	122.3(5)
C(20A)-C(19A)-C(21A)	107.7(5)	C(3B)-C(2B)-C(1B)	116.6(5)
C(22A)-C(19A)-C(21A)	107.3(5)	C(3B)-C(2B)-C(19B)	120.8(5)
C(2A)-C(19A)-C(21A)	112.0(5)	C(1B)-C(2B)-C(19B)	122.5(5)
C(26A)-C(23A)-C(24A)	106.2(6)	C(4B)-C(3B)-C(2B)	123.4(6)
C(26A)-C(23A)-C(25A)	112.1(6)	C(5B)-C(4B)-C(3B)	117.4(5)
C(24A)-C(23A)-C(25A)	107.9(6)	C(5B)-C(4B)-C(23B)	123.0(5)
C(26A)-C(23A)-C(4A)	111.1(5)	C(3B)-C(4B)-C(23B)	119.6(5)
C(24A)-C(23A)-C(4A)	111.2(5)	C(4B)-C(5B)-C(6B)	122.1(5)
C(25A)-C(23A)-C(4A)	108.2(5)	C(5B)-C(6B)-C(1B)	118.2(5)
C(30A)-C(27A)-C(29A)	111.2(5)	C(5B)-C(6B)-C(7B)	119.9(5)
C(30A)-C(27A)-C(28A)	108.0(5)	C(1B)-C(6B)-C(7B)	121.7(5)
C(29A)-C(27A)-C(28A)	105.2(5)	C(8B)-C(7B)-C(18B)	117.6(5)
C(30A)-C(27A)-C(14A)	111.8(5)	C(8B)-C(7B)-C(6B)	119.2(5)
C(29A)-C(27A)-C(14A)	108.7(4)	C(18B)-C(7B)-C(6B)	123.3(5)
C(28A)-C(27A)-C(14A)	111.7(5)	C(9B)-C(8B)-C(7B)	121.1(6)
C(16A)-C(31A)-C(33A)	111.2(5)	C(8B)-C(9B)-C(10B)	120.4(6)
C(16A)-C(31A)-C(32A)	111.9(5)	C(11B)-C(10B)-C(9B)	120.6(6)
C(33A)-C(31A)-C(32A)	107.3(5)	C(10B)-C(11B)-C(18B)	118.3(5)
C(16A)-C(31A)-C(34A)	110.2(5)	C(10B)-C(11B)-C(12B)	119.3(5)
C(33A)-C(31A)-C(34A)	109.9(5)	C(18B)-C(11B)-C(12B)	122.4(5)
C(32A)-C(31A)-C(34A)	106.1(5)	C(13B)-C(12B)-C(17B)	116.7(5)
O(2B)-Ta(2)-O(1B)	151.26(15)	C(13B)-C(12B)-C(11B)	121.1(5)
O(2B)-Ta(2)-C(35B)	102.75(17)	C(17B)-C(12B)-C(11B)	122.1(5)
O(1B)-Ta(2)-C(35B)	105.73(17)	C(14B)-C(13B)-C(12B)	122.8(5)
O(2B)-Ta(2)-Cl(1B)	91.09(12)	C(15B)-C(14B)-C(13B)	117.1(5)
O(1B)-Ta(2)-Cl(1B)	92.53(11)	C(15B)-C(14B)-C(27B)	121.7(5)
C(35B)-Ta(2)-Cl(1B)	90.34(14)	C(13B)-C(14B)-C(27B)	121.0(5)
O(2B)-Ta(2)-Cl(2B)	88.18(12)	C(14B)-C(15B)-C(16B)	123.9(5)

C(15B)-C(16B)-C(17B)	116.8(5)	C(28B)-C(27B)-C(29B)	111.1(7)
C(15B)-C(16B)-C(31B)	122.0(5)	C(28B)-C(27B)-C(30B)	107.3(6)
C(17B)-C(16B)-C(31B)	121.1(5)	C(29B)-C(27B)-C(30B)	108.0(6)
O(2B)-C(17B)-C(16B)	120.8(5)	C(28B)-C(27B)-C(14B)	110.9(5)
O(2B)-C(17B)-C(12B)	116.6(5)	C(29B)-C(27B)-C(14B)	108.8(5)
C(16B)-C(17B)-C(12B)	122.4(5)	C(30B)-C(27B)-C(14B)	110.7(5)
C(7B)-C(18B)-C(11B)	122.0(5)	C(32B)-C(31B)-C(34B)	107.1(5)
C(20B)-C(19B)-C(2B)	110.5(5)	C(32B)-C(31B)-C(33B)	107.2(5)
C(20B)-C(19B)-C(21B)	107.5(5)	C(34B)-C(31B)-C(33B)	110.1(5)
C(2B)-C(19B)-C(21B)	112.0(5)	C(32B)-C(31B)-C(16B)	112.0(5)
C(20B)-C(19B)-C(22B)	110.4(5)	C(34B)-C(31B)-C(16B)	109.9(4)
C(2B)-C(19B)-C(22B)	109.4(4)	C(33B)-C(31B)-C(16B)	110.5(5)
C(21B)-C(19B)-C(22B)	107.0(5)	C(3C)#1-C(1C)-C(2C)	120.4(10)
C(24B)-C(23B)-C(26B)	109.8(6)	C(3C)-C(2C)-C(1C)	119.6(10)
C(24B)-C(23B)-C(25B)	109.3(6)	C(1C)#1-C(3C)-C(2C)	120.1(11)
C(26B)-C(23B)-C(25B)	105.6(5)	C(2D)-C(1D)-C(3D)#2	120.6(9)
C(24B)-C(23B)-C(4B)	112.0(5)	C(1D)-C(2D)-C(3D)	118.8(9)
C(26B)-C(23B)-C(4B)	111.3(5)	C(1D)#2-C(3D)-C(2D)	120.6(9)
C(25B)-C(23B)-C(4B)	108.6(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y+2,-z

Table 5. Anisotropic displacement parameters ($Å^2 x 10^4$) for 4 (CCDC 626578). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta(1)	124(1)	198(2)	136(1)	2(1)	50(1)	13(1)
Cl(1A)	171(6)	243(8)	255(8)	-10(6)	-48(6)	10(6)
Cl(2A)	212(6)	266(9)	192(7)	0(6)	-25(6)	14(6)
O(1A)	79(10)	110(11)	122(10)	3(8)	74(8)	-6(8)
O(2A)	163(17)	190(20)	220(20)	-45(16)	-48(15)	0(16)
C(1A)	80(20)	240(30)	180(30)	-50(20)	0(20)	10(20)
C(2A)	120(20)	200(30)	130(30)	0(20)	-50(20)	20(20)
C(3A)	150(20)	170(30)	200(30)	0(20)	-50(20)	10(20)
C(4A)	160(20)	160(30)	260(30)	-30(20)	0(20)	10(20)
C(5A)	130(20)	310(40)	200(30)	-60(20)	60(20)	-20(20)
C(6A)	120(20)	120(30)	210(30)	-30(20)	10(20)	0(20)
C(7A)	140(20)	200(30)	90(20)	10(20)	34(19)	-10(20)
C(8A)	230(30)	160(30)	210(30)	-20(20)	40(20)	-40(20)
C(9A)	240(30)	290(40)	120(30)	-10(20)	-20(20)	-30(30)
C(10A)	240(30)	230(30)	150(30)	20(20)	10(20)	0(30)
C(11A)	100(20)	220(30)	190(30)	-20(20)	60(20)	20(20)
C(12A)	110(20)	200(30)	170(30)	40(20)	-10(20)	30(20)
C(13A)	140(20)	210(30)	190(30)	60(20)	-20(20)	0(20)
C(14A)	120(20)	210(30)	230(30)	60(20)	-50(20)	30(20)
C(15A)	210(30)	140(30)	240(30)	0(20)	-50(20)	-10(20)
C(16A)	160(20)	160(30)	210(30)	20(20)	-50(20)	10(20)
C(17A)	140(20)	210(30)	190(30)	40(20)	10(20)	-10(20)
C(18A)	90(20)	200(30)	160(30)	0(20)	50(20)	0(20)
C(19A)	200(30)	220(30)	140(30)	10(20)	0(20)	30(20)
C(20A)	250(30)	350(40)	170(30)	10(30)	-50(20)	10(30)
C(21A)	390(40)	220(40)	250(30)	50(30)	30(30)	40(30)
C(22A)	180(30)	320(40)	220(30)	30(30)	30(20)	-60(30)
C(23A)	190(30)	170(30)	290(30)	-50(20)	50(20)	30(20)
C(24A)	640(50)	340(50)	480(50)	40(40)	50(40)	300(40)
C(25A)	360(40)	640(60)	610(50)	-430(40)	-170(40)	160(40)

C(26A)	490(40)	220(40)	840(60)	-140(40)	390(40)	-20(30)
C(27A)	230(30)	190(30)	270(30)	80(20)	30(20)	-10(20)
C(28A)	460(40)	250(40)	530(50)	-30(30)	250(30)	-80(30)
C(29A)	250(30)	340(40)	390(40)	200(30)	-60(30)	-10(30)
C(30A)	420(40)	310(40)	510(50)	100(30)	-70(30)	-160(30)
C(31A)	250(30)	190(30)	190(30)	-10(20)	-20(20)	40(20)
C(32A)	490(40)	290(40)	210(30)	-80(30)	0(30)	10(30)
C(33A)	250(30)	310(40)	170(30)	50(30)	10(20)	20(30)
C(34A)	230(30)	330(40)	240(30)	-50(30)	0(20)	90(30)
C(35A)	150(20)	140(30)	70(20)	10(20)	28(19)	20(20)
Ta(2)	120(1)	197(2)	142(1)	-4(1)	46(1)	10(1)
Cl(1B)	185(6)	254(9)	272(8)	-8(6)	-52(6)	11(6)
Cl(2B)	190(6)	268(9)	199(7)	4(6)	-20(5)	23(6)
O(1B)	130(10)	96(11)	127(11)	-24(8)	56(8)	21(8)
O(2B)	243(19)	130(20)	154(19)	29(15)	38(15)	-16(16)
C(1B)	90(20)	270(30)	150(30)	50(20)	-33(19)	10(20)
C(2B)	100(20)	210(30)	200(30)	30(20)	0(20)	60(20)
C(3B)	150(20)	220(30)	260(30)	40(20)	-10(20)	40(20)
C(4B)	100(20)	200(30)	260(30)	70(20)	10(20)	30(20)
C(5B)	130(20)	240(30)	200(30)	50(20)	50(20)	30(20)
C(6B)	110(20)	170(30)	170(30)	40(20)	20(20)	30(20)
C(7B)	140(20)	190(30)	170(30)	40(20)	50(20)	10(20)
C(8B)	250(30)	200(30)	150(30)	60(20)	10(20)	40(20)
C(9B)	380(30)	180(30)	200(30)	-30(20)	0(30)	-10(30)
C(10B)	250(30)	290(40)	120(30)	-20(20)	-30(20)	0(30)
C(11B)	110(20)	210(30)	210(30)	10(20)	40(20)	50(20)
C(12B)	110(20)	250(30)	110(20)	-10(20)	0(19)	-10(20)
C(13B)	120(20)	260(30)	160(30)	-60(20)	10(20)	10(20)
C(14B)	100(20)	170(30)	260(30)	-70(20)	-30(20)	30(20)
C(15B)	200(30)	200(30)	160(30)	-20(20)	-90(20)	0(20)
C(16B)	150(20)	220(30)	160(30)	0(20)	-40(20)	20(20)
C(17B)	140(20)	190(30)	150(30)	-10(20)	-30(20)	-20(20)
C(18B)	140(20)	200(30)	90(20)	20(20)	20(20)	70(20)
C(19B)	180(20)	300(40)	110(30)	-10(20)	-10(20)	-20(20)
C(20B)	220(30)	330(40)	160(30)	10(30)	0(20)	20(30)

C(21B)	440(40)	300(40)	220(30)	-10(30)	50(30)	-10(30)
C(22B)	160(30)	430(40)	200(30)	-30(30)	20(20)	80(30)
C(23B)	140(20)	200(30)	380(40)	70(30)	60(20)	20(20)
C(24B)	490(40)	410(50)	580(50)	280(40)	-200(40)	-280(40)
C(25B)	280(30)	270(40)	330(40)	80(30)	-100(30)	-60(30)
C(26B)	490(40)	220(40)	750(60)	50(40)	430(40)	-40(30)
C(27B)	160(20)	240(30)	320(30)	-60(30)	20(20)	20(20)
C(28B)	690(60)	180(40)	1490(90)	-190(50)	830(60)	-10(40)
C(29B)	470(40)	410(50)	550(50)	-290(40)	-210(40)	250(40)
C(30B)	640(50)	440(50)	510(50)	-40(40)	-110(40)	370(40)
C(31B)	200(30)	200(30)	170(30)	-20(20)	10(20)	-30(20)
C(32B)	420(40)	230(40)	270(30)	40(30)	30(30)	30(30)
C(33B)	220(30)	260(40)	280(30)	30(30)	-20(20)	-40(30)
C(34B)	270(30)	330(40)	120(30)	20(20)	-10(20)	-10(30)
C(35B)	140(20)	100(30)	100(20)	-7(19)	20(19)	-30(20)
C(1C)	380(50)	1460(120)	460(60)	150(70)	150(40)	-120(70)
C(2C)	400(50)	1600(130)	530(60)	-300(80)	260(40)	-340(70)
C(3C)	500(50)	890(80)	850(80)	150(70)	420(50)	50(50)
C(1D)	490(50)	580(60)	1030(80)	-300(60)	390(50)	-90(50)
C(2D)	400(50)	1000(90)	570(60)	260(60)	70(40)	50(50)
C(3D)	390(40)	1290(100)	310(50)	-130(60)	80(40)	-160(60)

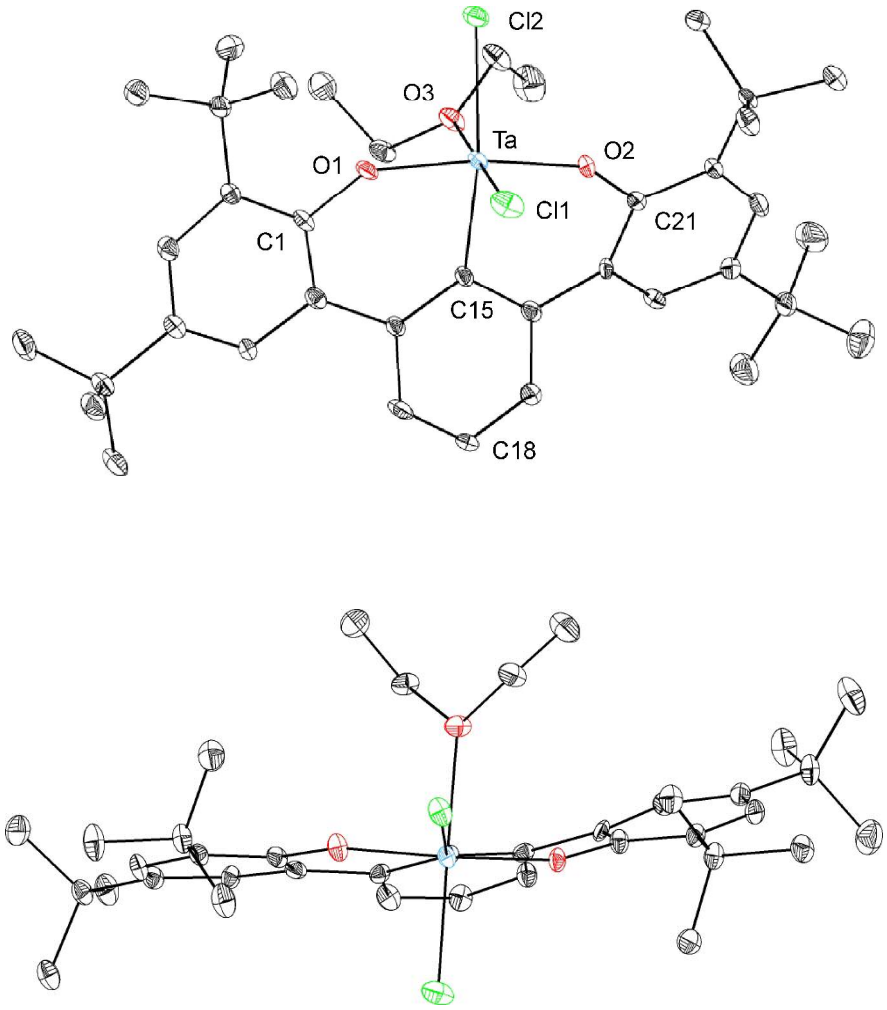


Figure 5. Structural drawing of **5-OEt$_2$** with displacement ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ta-O1 1.8828(13); Ta-O2 1.8755(13); Ta-O3 2.2446(14); Ta-C15 2.1870(19); Ta-C15-C18 164.2; O1-Ta-O2 168.75(6); C21-O2-Ta 145.34(13); C1-O1-Ta 142.51(13).

Special Refinement Details for 5-OEt$_2$

Residual peaks in the final electron density difference Fourier map lie near the metal centers. Absorption corrections did not appreciably account for these peaks therefore the corrections were not applied.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 5-OEt$_2$ (CCDC 601396). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ta(1)	275(1)	-352(1)	2674(1)	9(1)
Cl(1A)	801(1)	-1652(1)	2073(1)	21(1)
Cl(2A)	-171(1)	-874(1)	3898(1)	15(1)
O(1A)	-863(1)	-535(1)	2046(1)	13(1)
O(2A)	1425(1)	31(1)	3192(1)	13(1)
O(3A)	-250(1)	914(1)	3222(1)	14(1)
C(1A)	-1447(1)	-155(1)	1505(1)	11(1)
C(2A)	-2355(1)	-464(1)	1366(1)	12(1)
C(3A)	-2925(1)	-4(1)	840(1)	14(1)
C(4A)	-2626(1)	724(1)	465(1)	13(1)
C(5A)	-1718(1)	977(1)	606(1)	13(1)
C(6A)	-1091(1)	525(1)	1103(1)	12(1)
C(7A)	-2704(1)	-1272(1)	1754(1)	13(1)
C(8A)	-2185(1)	-2098(1)	1506(1)	17(1)
C(9A)	-2606(1)	-1088(2)	2693(1)	18(1)

C(10A)	-3707(1)	-1495(1)	1463(1)	18(1)
C(11A)	-3304(1)	1180(1)	-111(1)	15(1)
C(12A)	-3673(2)	519(2)	-842(2)	28(1)
C(13A)	-4099(2)	1488(2)	351(2)	26(1)
C(14A)	-2898(2)	1990(2)	-420(2)	25(1)
C(15A)	582(1)	548(1)	1780(1)	10(1)
C(16A)	-103(1)	723(1)	1131(1)	11(1)
C(17A)	148(1)	1076(1)	433(1)	13(1)
C(18A)	1033(1)	1279(1)	364(1)	15(1)
C(19A)	1698(1)	1165(1)	994(1)	14(1)
C(20A)	1496(1)	836(1)	1721(1)	11(1)
C(21A)	2227(1)	408(1)	3097(1)	12(1)
C(22A)	2959(1)	361(1)	3714(1)	13(1)
C(23A)	3777(1)	740(1)	3581(1)	14(1)
C(24A)	3878(1)	1183(1)	2890(1)	14(1)
C(25A)	3128(1)	1226(1)	2313(1)	13(1)
C(26A)	2283(1)	817(1)	2378(1)	11(1)
C(27A)	2846(1)	-72(1)	4499(1)	15(1)
C(28A)	2186(2)	440(2)	4984(1)	21(1)
C(29A)	3743(2)	-72(2)	5056(1)	23(1)
C(30A)	2493(2)	-1055(2)	4301(2)	21(1)
C(31A)	4812(1)	1567(1)	2785(1)	14(1)
C(32A)	5239(1)	2133(2)	3567(1)	21(1)
C(33A)	4774(1)	2153(2)	2081(2)	20(1)
C(34A)	5416(1)	785(2)	2604(2)	20(1)
C(35A)	295(1)	1752(1)	3359(1)	16(1)
C(36A)	500(2)	2091(2)	4249(1)	20(1)
C(37A)	-1115(1)	967(1)	3529(1)	18(1)
C(38A)	-1697(2)	1658(2)	3163(2)	29(1)

Ta(2)	138(1)	4671(1)	2571(1)	9(1)
Cl(1B)	214(1)	3314(1)	1791(1)	18(1)
Cl(2B)	-375(1)	4120(1)	3759(1)	16(1)
O(1B)	-1037(1)	4823(1)	2098(1)	13(1)
O(2B)	1386(1)	4717(1)	2940(1)	12(1)
O(3B)	97(1)	5957(1)	3346(1)	16(1)
C(1B)	-1562(1)	5106(1)	1459(1)	12(1)
C(2B)	-2499(1)	4911(1)	1387(1)	14(1)
C(3B)	-3005(1)	5193(1)	700(1)	16(1)
C(4B)	-2619(1)	5645(1)	126(1)	15(1)
C(5B)	-1699(1)	5832(1)	241(1)	14(1)
C(6B)	-1134(1)	5557(1)	913(1)	12(1)
C(7B)	-2927(1)	4408(1)	2004(1)	17(1)
C(8B)	-2733(2)	4902(2)	2869(2)	24(1)
C(9B)	-2572(2)	3456(2)	2014(2)	25(1)
C(10B)	-3956(2)	4317(2)	1800(2)	25(1)
C(11B)	-3230(1)	5928(2)	-610(1)	18(1)
C(12B)	-3910(2)	6580(2)	-300(2)	24(1)
C(13B)	-3746(2)	5110(2)	-1088(1)	24(1)
C(14B)	-2695(2)	6371(2)	-1198(2)	29(1)
C(15B)	484(1)	5592(1)	1709(1)	9(1)
C(16B)	-137(1)	5748(1)	1009(1)	11(1)
C(17B)	195(1)	6127(1)	357(1)	14(1)
C(18B)	1089(1)	6382(1)	379(1)	15(1)
C(19B)	1682(1)	6306(1)	1076(1)	12(1)
C(20B)	1396(1)	5939(1)	1750(1)	10(1)
C(21B)	2134(1)	5257(1)	2993(1)	11(1)
C(22B)	2892(1)	5128(1)	3566(1)	13(1)
C(23B)	3608(1)	5752(1)	3617(1)	14(1)
C(24B)	3600(1)	6479(1)	3149(1)	13(1)
C(25B)	2851(1)	6548(1)	2579(1)	12(1)
C(26B)	2120(1)	5919(1)	2460(1)	11(1)
C(27B)	2924(1)	4340(1)	4086(1)	16(1)
C(28B)	2801(2)	3459(2)	3521(2)	22(1)
C(29B)	3839(2)	4328(2)	4619(2)	26(1)
C(30B)	2192(2)	4381(2)	4663(1)	21(1)

C(31B)	4429(1)	7120(1)	3259(1)	16(1)
C(32B)	4666(2)	7479(2)	4162(1)	21(1)
C(33B)	4294(2)	7909(2)	2748(2)	22(1)
C(34B)	5229(2)	6607(2)	2977(2)	27(1)
C(35B)	539(2)	6122(1)	4191(1)	18(1)
C(36B)	1194(2)	6921(2)	4325(2)	24(1)
C(37B)	-437(2)	6691(1)	3076(1)	17(1)
C(38B)	-1178(2)	6896(2)	3591(2)	22(1)

Table 7. Selected bond lengths [Å] and angles [°] for 5-OEt$_2$ (CCDC 601396).

Ta(1)-O(2A)	1.8755(13)	Ta(2)-O(1B)	1.8708(13)
Ta(1)-O(1A)	1.8828(13)	Ta(2)-O(2B)	1.8926(13)
Ta(1)-C(15A)	2.1870(19)	Ta(2)-C(15B)	2.1854(18)
Ta(1)-O(3A)	2.2446(14)	Ta(2)-O(3B)	2.2277(14)
Ta(1)-Cl(1A)	2.3219(5)	Ta(2)-Cl(1B)	2.3265(5)
Ta(1)-Cl(2A)	2.4062(5)	Ta(2)-Cl(2B)	2.4108(5)
O(2A)-Ta(1)-O(1A)	168.75(6)	O(1B)-Ta(2)-O(2B)	168.45(6)
O(2A)-Ta(1)-C(15A)	83.66(6)	O(1B)-Ta(2)-C(15B)	83.15(6)
O(1A)-Ta(1)-C(15A)	85.64(6)	O(2B)-Ta(2)-C(15B)	85.59(6)
O(2A)-Ta(1)-O(3A)	88.61(6)	O(1B)-Ta(2)-O(3B)	89.11(6)
O(1A)-Ta(1)-O(3A)	86.07(6)	O(2B)-Ta(2)-O(3B)	86.46(6)
C(15A)-Ta(1)-O(3A)	79.81(6)	C(15B)-Ta(2)-O(3B)	80.30(6)
O(2A)-Ta(1)-Cl(1A)	92.28(5)	O(1B)-Ta(2)-Cl(1B)	92.46(5)
O(1A)-Ta(1)-Cl(1A)	92.84(5)	O(2B)-Ta(2)-Cl(1B)	92.13(5)
C(15A)-Ta(1)-Cl(1A)	99.03(5)	C(15B)-Ta(2)-Cl(1B)	100.59(5)
O(3A)-Ta(1)-Cl(1A)	178.46(4)	O(3B)-Ta(2)-Cl(1B)	178.28(4)
O(2A)-Ta(1)-Cl(2A)	92.77(5)	O(1B)-Ta(2)-Cl(2B)	92.27(5)
O(1A)-Ta(1)-Cl(2A)	96.19(5)	O(2B)-Ta(2)-Cl(2B)	97.53(5)
C(15A)-Ta(1)-Cl(2A)	160.73(5)	C(15B)-Ta(2)-Cl(2B)	160.55(5)
O(3A)-Ta(1)-Cl(2A)	81.17(4)	O(3B)-Ta(2)-Cl(2B)	80.74(4)
Cl(1A)-Ta(1)-Cl(2A)	100.032(19)	Cl(1B)-Ta(2)-Cl(2B)	98.481(18)

Table 8. Bond lengths [Å] and angles [°] for 5-OEt_2 (CCDC 601396).

Ta(1)-O(2A)	1.8755(13)	C(22A)-C(23A)	1.388(3)
Ta(1)-O(1A)	1.8828(13)	C(22A)-C(27A)	1.538(3)
Ta(1)-C(15A)	2.1870(19)	C(23A)-C(24A)	1.402(3)
Ta(1)-O(3A)	2.2446(14)	C(24A)-C(25A)	1.392(2)
Ta(1)-Cl(1A)	2.3219(5)	C(24A)-C(31A)	1.534(3)
Ta(1)-Cl(2A)	2.4062(5)	C(25A)-C(26A)	1.412(3)
O(1A)-C(1A)	1.358(2)	C(27A)-C(28A)	1.532(3)
O(2A)-C(21A)	1.347(2)	C(27A)-C(29A)	1.535(3)
O(3A)-C(37A)	1.452(2)	C(27A)-C(30A)	1.549(3)
O(3A)-C(35A)	1.467(2)	C(31A)-C(33A)	1.531(3)
C(1A)-C(6A)	1.405(3)	C(31A)-C(32A)	1.536(3)
C(1A)-C(2A)	1.409(2)	C(31A)-C(34A)	1.542(3)
C(2A)-C(3A)	1.398(3)	C(35A)-C(36A)	1.503(3)
C(2A)-C(7A)	1.541(3)	C(37A)-C(38A)	1.511(3)
C(3A)-C(4A)	1.403(3)	Ta(2)-O(1B)	1.8708(13)
C(4A)-C(5A)	1.386(2)	Ta(2)-O(2B)	1.8926(13)
C(4A)-C(11A)	1.537(2)	Ta(2)-C(15B)	2.1854(18)
C(5A)-C(6A)	1.412(2)	Ta(2)-O(3B)	2.2277(14)
C(6A)-C(16A)	1.496(2)	Ta(2)-Cl(1B)	2.3265(5)
C(7A)-C(10A)	1.537(3)	Ta(2)-Cl(2B)	2.4108(5)
C(7A)-C(9A)	1.540(3)	O(1B)-C(1B)	1.355(2)
C(7A)-C(8A)	1.542(3)	O(2B)-C(21B)	1.354(2)
C(11A)-C(14A)	1.512(3)	O(3B)-C(37B)	1.466(2)
C(11A)-C(12A)	1.526(3)	O(3B)-C(35B)	1.467(2)
C(11A)-C(13A)	1.554(3)	C(1B)-C(6B)	1.389(3)
C(15A)-C(20A)	1.442(2)	C(1B)-C(2B)	1.413(3)
C(15A)-C(16A)	1.443(2)	C(2B)-C(3B)	1.400(3)
C(16A)-C(17A)	1.406(3)	C(2B)-C(7B)	1.523(3)
C(17A)-C(18A)	1.373(3)	C(3B)-C(4B)	1.395(3)
C(18A)-C(19A)	1.381(3)	C(4B)-C(5B)	1.385(3)
C(19A)-C(20A)	1.410(3)	C(4B)-C(11B)	1.538(3)
C(20A)-C(26A)	1.507(2)	C(5B)-C(6B)	1.419(2)
C(21A)-C(26A)	1.405(3)	C(6B)-C(16B)	1.499(2)
C(21A)-C(22A)	1.415(2)	C(7B)-C(8B)	1.537(3)

C(7B)-C(10B)	1.538(3)	O(1A)-Ta(1)-Cl(1A)	92.84(5)
C(7B)-C(9B)	1.552(3)	C(15A)-Ta(1)-Cl(1A)	99.03(5)
C(11B)-C(14B)	1.526(4)	O(3A)-Ta(1)-Cl(1A)	178.46(4)
C(11B)-C(13B)	1.531(3)	O(2A)-Ta(1)-Cl(2A)	92.77(5)
C(11B)-C(12B)	1.540(3)	O(1A)-Ta(1)-Cl(2A)	96.19(5)
C(15B)-C(20B)	1.439(2)	C(15A)-Ta(1)-Cl(2A)	160.73(5)
C(15B)-C(16B)	1.440(2)	O(3A)-Ta(1)-Cl(2A)	81.17(4)
C(16B)-C(17B)	1.406(3)	Cl(1A)-Ta(1)-Cl(2A)	100.032(19)
C(17B)-C(18B)	1.377(3)	C(1A)-O(1A)-Ta(1)	142.51(13)
C(18B)-C(19B)	1.385(2)	C(21A)-O(2A)-Ta(1)	145.34(13)
C(19B)-C(20B)	1.401(3)	C(37A)-O(3A)-C(35A)	114.10(15)
C(20B)-C(26B)	1.503(2)	C(37A)-O(3A)-Ta(1)	123.84(12)
C(21B)-C(26B)	1.398(3)	C(35A)-O(3A)-Ta(1)	121.90(12)
C(21B)-C(22B)	1.421(2)	O(1A)-C(1A)-C(6A)	116.70(15)
C(22B)-C(23B)	1.393(3)	O(1A)-C(1A)-C(2A)	119.48(17)
C(22B)-C(27B)	1.537(3)	C(6A)-C(1A)-C(2A)	123.82(16)
C(23B)-C(24B)	1.407(3)	C(3A)-C(2A)-C(1A)	116.03(17)
C(24B)-C(25B)	1.391(2)	C(3A)-C(2A)-C(7A)	121.55(16)
C(24B)-C(31B)	1.531(3)	C(1A)-C(2A)-C(7A)	122.41(16)
C(25B)-C(26B)	1.408(3)	C(2A)-C(3A)-C(4A)	122.95(17)
C(27B)-C(30B)	1.540(3)	C(5A)-C(4A)-C(3A)	118.15(17)
C(27B)-C(29B)	1.540(3)	C(5A)-C(4A)-C(11A)	122.82(18)
C(27B)-C(28B)	1.542(3)	C(3A)-C(4A)-C(11A)	118.98(16)
C(31B)-C(32B)	1.533(3)	C(4A)-C(5A)-C(6A)	122.50(18)
C(31B)-C(33B)	1.536(3)	C(1A)-C(6A)-C(5A)	116.19(16)
C(31B)-C(34B)	1.546(3)	C(1A)-C(6A)-C(16A)	122.96(16)
C(35B)-C(36B)	1.511(3)	C(5A)-C(6A)-C(16A)	120.66(17)
C(37B)-C(38B)	1.504(3)	C(10A)-C(7A)-C(9A)	106.89(17)
		C(10A)-C(7A)-C(2A)	111.50(16)
O(2A)-Ta(1)-O(1A)	168.75(6)	C(9A)-C(7A)-C(2A)	111.09(16)
O(2A)-Ta(1)-C(15A)	83.66(6)	C(10A)-C(7A)-C(8A)	107.45(16)
O(1A)-Ta(1)-C(15A)	85.64(6)	C(9A)-C(7A)-C(8A)	109.92(16)
O(2A)-Ta(1)-O(3A)	88.61(6)	C(2A)-C(7A)-C(8A)	109.87(17)
O(1A)-Ta(1)-O(3A)	86.07(6)	C(14A)-C(11A)-C(12A)	108.8(2)
C(15A)-Ta(1)-O(3A)	79.81(6)	C(14A)-C(11A)-C(4A)	112.87(16)
O(2A)-Ta(1)-Cl(1A)	92.28(5)	C(12A)-C(11A)-C(4A)	109.39(17)

C(14A)-C(11A)-C(13A)	107.56(19)	C(33A)-C(31A)-C(32A)	107.85(18)
C(12A)-C(11A)-C(13A)	108.55(19)	C(24A)-C(31A)-C(32A)	111.04(17)
C(4A)-C(11A)-C(13A)	109.56(18)	C(33A)-C(31A)-C(34A)	108.86(18)
C(20A)-C(15A)-C(16A)	117.70(16)	C(24A)-C(31A)-C(34A)	108.31(16)
C(20A)-C(15A)-Ta(1)	121.08(12)	C(32A)-C(31A)-C(34A)	108.78(16)
C(16A)-C(15A)-Ta(1)	120.11(13)	O(3A)-C(35A)-C(36A)	112.78(18)
C(17A)-C(16A)-C(15A)	119.67(16)	O(3A)-C(37A)-C(38A)	113.4(2)
C(17A)-C(16A)-C(6A)	114.47(15)	O(1B)-Ta(2)-O(2B)	168.45(6)
C(15A)-C(16A)-C(6A)	125.80(17)	O(1B)-Ta(2)-C(15B)	83.15(6)
C(18A)-C(17A)-C(16A)	121.27(17)	O(2B)-Ta(2)-C(15B)	85.59(6)
C(17A)-C(18A)-C(19A)	120.38(19)	O(1B)-Ta(2)-O(3B)	89.11(6)
C(18A)-C(19A)-C(20A)	121.57(17)	O(2B)-Ta(2)-O(3B)	86.46(6)
C(19A)-C(20A)-C(15A)	118.94(15)	C(15B)-Ta(2)-O(3B)	80.30(6)
C(19A)-C(20A)-C(26A)	115.35(16)	O(1B)-Ta(2)-Cl(1B)	92.46(5)
C(15A)-C(20A)-C(26A)	125.71(17)	O(2B)-Ta(2)-Cl(1B)	92.13(5)
O(2A)-C(21A)-C(26A)	117.42(15)	C(15B)-Ta(2)-Cl(1B)	100.59(5)
O(2A)-C(21A)-C(22A)	118.53(17)	O(3B)-Ta(2)-Cl(1B)	178.28(4)
C(26A)-C(21A)-C(22A)	124.05(17)	O(1B)-Ta(2)-Cl(2B)	92.27(5)
C(23A)-C(22A)-C(21A)	116.57(18)	O(2B)-Ta(2)-Cl(2B)	97.53(5)
C(23A)-C(22A)-C(27A)	121.92(16)	C(15B)-Ta(2)-Cl(2B)	160.55(5)
C(21A)-C(22A)-C(27A)	121.50(16)	O(3B)-Ta(2)-Cl(2B)	80.74(4)
C(22A)-C(23A)-C(24A)	122.55(16)	Cl(1B)-Ta(2)-Cl(2B)	98.481(18)
C(25A)-C(24A)-C(23A)	118.25(17)	C(1B)-O(1B)-Ta(2)	146.05(14)
C(25A)-C(24A)-C(31A)	122.74(18)	C(21B)-O(2B)-Ta(2)	141.34(12)
C(23A)-C(24A)-C(31A)	118.97(16)	C(37B)-O(3B)-C(35B)	113.83(15)
C(24A)-C(25A)-C(26A)	122.87(18)	C(37B)-O(3B)-Ta(2)	122.60(11)
C(21A)-C(26A)-C(25A)	115.57(15)	C(35B)-O(3B)-Ta(2)	123.40(11)
C(21A)-C(26A)-C(20A)	122.80(16)	O(1B)-C(1B)-C(6B)	117.19(16)
C(25A)-C(26A)-C(20A)	121.63(17)	O(1B)-C(1B)-C(2B)	117.96(18)
C(28A)-C(27A)-C(29A)	107.76(18)	C(6B)-C(1B)-C(2B)	124.84(16)
C(28A)-C(27A)-C(22A)	110.18(17)	C(3B)-C(2B)-C(1B)	115.53(19)
C(29A)-C(27A)-C(22A)	111.54(17)	C(3B)-C(2B)-C(7B)	122.14(17)
C(28A)-C(27A)-C(30A)	108.90(19)	C(1B)-C(2B)-C(7B)	122.31(16)
C(29A)-C(27A)-C(30A)	107.00(17)	C(4B)-C(3B)-C(2B)	122.65(18)
C(22A)-C(27A)-C(30A)	111.32(17)	C(5B)-C(4B)-C(3B)	118.91(17)
C(33A)-C(31A)-C(24A)	111.95(15)	C(5B)-C(4B)-C(11B)	122.2(2)

C(3B)-C(4B)-C(11B)	118.87(17)	O(2B)-C(21B)-C(26B)	117.09(15)
C(4B)-C(5B)-C(6B)	122.1(2)	O(2B)-C(21B)-C(22B)	119.82(17)
C(1B)-C(6B)-C(5B)	115.94(16)	C(26B)-C(21B)-C(22B)	123.09(17)
C(1B)-C(6B)-C(16B)	123.21(15)	C(23B)-C(22B)-C(21B)	115.79(17)
C(5B)-C(6B)-C(16B)	120.85(18)	C(23B)-C(22B)-C(27B)	122.25(16)
C(2B)-C(7B)-C(8B)	111.04(18)	C(21B)-C(22B)-C(27B)	121.95(17)
C(2B)-C(7B)-C(10B)	111.58(17)	C(22B)-C(23B)-C(24B)	123.63(16)
C(8B)-C(7B)-C(10B)	106.40(19)	C(25B)-C(24B)-C(23B)	117.60(17)
C(2B)-C(7B)-C(9B)	110.63(19)	C(25B)-C(24B)-C(31B)	123.56(18)
C(8B)-C(7B)-C(9B)	109.26(18)	C(23B)-C(24B)-C(31B)	118.76(16)
C(10B)-C(7B)-C(9B)	107.77(17)	C(24B)-C(25B)-C(26B)	122.21(18)
C(14B)-C(11B)-C(13B)	107.6(2)	C(21B)-C(26B)-C(25B)	117.22(15)
C(14B)-C(11B)-C(4B)	112.02(17)	C(21B)-C(26B)-C(20B)	122.51(16)
C(13B)-C(11B)-C(4B)	109.72(18)	C(25B)-C(26B)-C(20B)	120.15(17)
C(14B)-C(11B)-C(12B)	109.2(2)	C(22B)-C(27B)-C(30B)	111.56(17)
C(13B)-C(11B)-C(12B)	108.96(18)	C(22B)-C(27B)-C(29B)	111.33(18)
C(4B)-C(11B)-C(12B)	109.31(17)	C(30B)-C(27B)-C(29B)	107.53(18)
C(20B)-C(15B)-C(16B)	117.63(16)	C(22B)-C(27B)-C(28B)	109.67(17)
C(20B)-C(15B)-Ta(2)	119.93(12)	C(30B)-C(27B)-C(28B)	109.52(19)
C(16B)-C(15B)-Ta(2)	121.58(13)	C(29B)-C(27B)-C(28B)	107.11(18)
C(17B)-C(16B)-C(15B)	118.84(16)	C(24B)-C(31B)-C(32B)	110.29(18)
C(17B)-C(16B)-C(6B)	115.73(15)	C(24B)-C(31B)-C(33B)	112.50(16)
C(15B)-C(16B)-C(6B)	125.41(17)	C(32B)-C(31B)-C(33B)	108.82(18)
C(18B)-C(17B)-C(16B)	122.15(17)	C(24B)-C(31B)-C(34B)	108.57(18)
C(17B)-C(18B)-C(19B)	119.80(19)	C(32B)-C(31B)-C(34B)	108.83(18)
C(18B)-C(19B)-C(20B)	120.99(17)	C(33B)-C(31B)-C(34B)	107.7(2)
C(19B)-C(20B)-C(15B)	120.01(15)	O(3B)-C(35B)-C(36B)	112.95(19)
C(19B)-C(20B)-C(26B)	114.25(15)	O(3B)-C(37B)-C(38B)	112.60(18)
C(15B)-C(20B)-C(26B)	125.70(16)		

Table 9. Anisotropic displacement parameters ($Å^2 x 10^4$) for 5-OEt_2 (CCDC 601396). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta(1)	73(1)	97(1)	100(1)	29(1)	12(1)	-2(1)
Cl(1A)	245(2)	143(2)	274(3)	21(2)	108(2)	52(2)
Cl(2A)	139(2)	185(2)	147(2)	76(2)	36(1)	8(1)
O(1A)	100(5)	152(6)	122(5)	47(5)	-4(4)	-17(4)
O(2A)	76(4)	182(6)	144(6)	85(5)	7(4)	-14(4)
O(3A)	139(5)	104(5)	186(6)	-3(5)	74(5)	-17(4)
C(1A)	89(6)	138(7)	109(7)	23(6)	2(5)	-14(5)
C(2A)	96(6)	138(7)	112(7)	14(6)	3(5)	-29(5)
C(3A)	93(6)	165(8)	159(8)	21(7)	-6(6)	-17(5)
C(4A)	102(6)	157(7)	116(7)	33(6)	-6(5)	-9(5)
C(5A)	100(6)	160(7)	129(7)	45(6)	3(5)	-12(5)
C(6A)	87(6)	144(7)	108(7)	6(6)	-7(5)	-19(5)
C(7A)	106(6)	144(7)	144(7)	21(6)	6(5)	-26(5)
C(8A)	149(7)	130(7)	230(9)	0(7)	30(7)	-13(6)
C(9A)	162(8)	211(9)	155(8)	38(7)	22(6)	-25(6)
C(10A)	116(7)	195(8)	213(9)	36(8)	21(6)	-39(6)
C(11A)	125(7)	182(8)	145(8)	53(7)	-28(6)	-8(6)
C(12A)	284(12)	279(12)	241(11)	38(10)	-101(9)	-1(9)
C(13A)	158(8)	326(12)	303(12)	110(10)	36(8)	58(8)
C(14A)	178(9)	284(11)	281(12)	124(10)	-27(8)	-30(8)
C(15A)	90(5)	113(6)	94(6)	10(6)	5(5)	-5(5)
C(16A)	95(6)	128(7)	90(6)	6(6)	10(5)	-13(5)
C(17A)	115(6)	180(8)	106(7)	32(7)	6(5)	-10(5)
C(18A)	125(7)	226(9)	103(7)	51(7)	22(6)	-26(6)
C(19A)	103(6)	212(9)	125(7)	42(7)	22(5)	-25(6)
C(20A)	92(6)	133(7)	105(7)	22(6)	9(5)	-4(5)
C(21A)	78(5)	147(7)	124(7)	32(6)	14(5)	1(5)
C(22A)	92(6)	159(7)	124(7)	36(6)	-2(5)	-7(5)

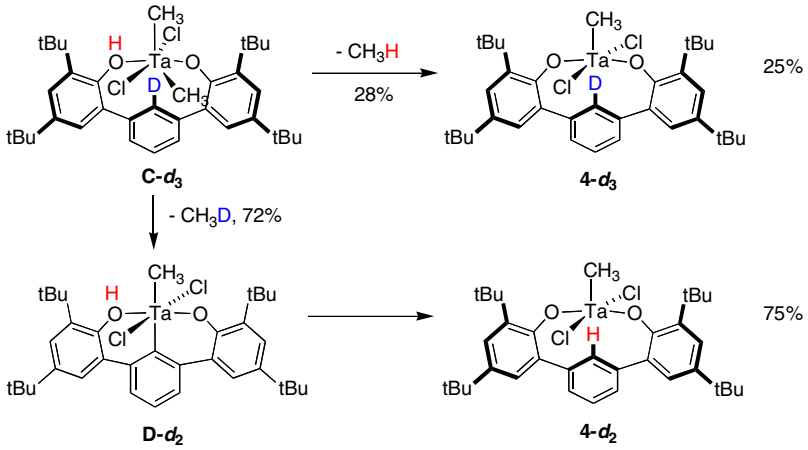
C(23A)	91(6)	166(8)	151(8)	39(7)	-1(5)	5(5)
C(24A)	86(6)	164(7)	155(8)	31(7)	2(5)	-2(5)
C(25A)	89(6)	161(7)	128(7)	32(6)	3(5)	-12(5)
C(26A)	88(6)	128(7)	109(7)	13(6)	10(5)	0(5)
C(27A)	114(6)	202(8)	142(8)	68(7)	-8(6)	-1(6)
C(28A)	191(9)	299(11)	163(9)	57(9)	42(7)	19(8)
C(29A)	160(8)	330(12)	203(10)	124(9)	-49(7)	-31(8)
C(30A)	171(8)	210(9)	266(11)	128(9)	-17(8)	5(7)
C(31A)	95(6)	159(7)	168(8)	32(7)	11(6)	-5(5)
C(32A)	152(8)	228(10)	237(10)	-25(9)	-1(7)	-67(7)
C(33A)	128(7)	236(10)	259(10)	103(9)	18(7)	-26(6)
C(34A)	108(7)	231(9)	253(10)	41(8)	37(7)	27(6)
C(35A)	196(8)	124(7)	166(8)	-2(7)	60(7)	-31(6)
C(36A)	249(10)	158(8)	184(9)	-4(8)	5(8)	-2(7)
C(37A)	145(7)	151(8)	255(10)	16(8)	84(7)	15(6)
C(38A)	217(10)	262(11)	383(14)	39(11)	15(10)	92(8)

Ta(2)	81(1)	99(1)	79(1)	26(1)	-9(1)	-2(1)
Cl(1B)	274(2)	123(2)	133(2)	4(2)	13(2)	4(2)
Cl(2B)	173(2)	182(2)	120(2)	62(2)	21(2)	-15(1)
O(1B)	106(5)	167(6)	126(6)	67(5)	-28(4)	-17(4)
O(2B)	98(5)	147(6)	124(5)	54(5)	-22(4)	3(4)
O(3B)	269(7)	138(6)	76(5)	23(5)	-4(5)	64(5)
C(1B)	95(6)	144(7)	116(7)	17(6)	-32(5)	5(5)
C(2B)	99(6)	151(7)	176(8)	30(7)	-28(6)	4(5)
C(3B)	99(6)	181(8)	172(8)	2(7)	-48(6)	17(5)
C(4B)	108(6)	177(8)	150(8)	8(7)	-45(6)	25(5)
C(5B)	111(6)	176(8)	127(7)	27(7)	-25(5)	26(5)
C(6B)	98(6)	135(7)	112(7)	13(6)	-24(5)	7(5)
C(7B)	102(6)	178(8)	215(9)	49(7)	-15(6)	-29(5)
C(8B)	160(8)	324(12)	222(10)	38(9)	31(7)	-12(8)
C(9B)	189(9)	186(9)	359(13)	101(9)	-40(9)	-34(7)
C(10B)	121(8)	285(11)	358(13)	121(10)	-17(8)	-57(7)
C(11B)	126(7)	247(9)	146(8)	30(8)	-37(6)	59(6)

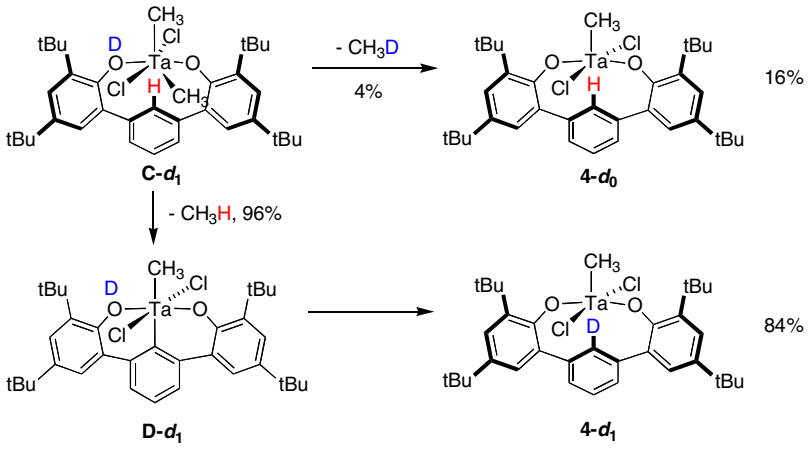
C(12B)	220(9)	268(11)	220(10)	-10(9)	-57(8)	124(8)
C(13B)	182(9)	293(11)	206(10)	-53(9)	-88(7)	62(8)
C(14B)	197(10)	443(15)	221(11)	138(11)	-54(8)	67(9)
C(15B)	92(5)	99(6)	83(6)	24(6)	6(5)	11(4)
C(16B)	89(6)	137(7)	87(6)	9(6)	-15(5)	4(5)
C(17B)	122(7)	212(9)	102(7)	49(7)	-13(6)	-2(6)
C(18B)	146(7)	213(9)	102(7)	64(7)	3(6)	-9(6)
C(19B)	110(6)	156(7)	100(7)	38(6)	3(5)	-1(5)
C(20B)	88(5)	119(6)	81(6)	24(6)	-4(5)	4(5)
C(21B)	84(5)	148(7)	98(6)	26(6)	-3(5)	9(5)
C(22B)	100(6)	169(8)	121(7)	52(7)	-18(5)	22(5)
C(23B)	108(6)	187(8)	123(7)	37(7)	-22(5)	7(5)
C(24B)	99(6)	161(7)	127(7)	4(6)	-12(5)	-9(5)
C(25B)	114(6)	146(7)	106(7)	23(6)	-9(5)	2(5)
C(26B)	81(5)	134(7)	98(6)	17(6)	-8(5)	14(5)
C(27B)	131(7)	190(8)	170(8)	80(7)	-31(6)	15(6)
C(28B)	258(10)	174(9)	231(10)	65(8)	-17(8)	62(7)
C(29B)	162(9)	332(12)	275(11)	170(10)	-75(8)	20(8)
C(30B)	190(9)	276(11)	171(9)	112(9)	8(7)	17(7)
C(31B)	111(6)	194(8)	162(8)	6(7)	-2(6)	-32(6)
C(32B)	216(9)	189(9)	193(9)	-8(8)	-67(8)	-16(7)
C(33B)	182(9)	252(10)	229(10)	76(9)	-15(8)	-77(7)
C(34B)	147(8)	287(12)	369(13)	1(11)	66(9)	-3(7)
C(35B)	275(10)	151(8)	104(7)	1(7)	-36(7)	18(7)
C(36B)	259(10)	212(10)	237(10)	-55(9)	24(8)	-36(8)
C(37B)	262(9)	130(7)	125(8)	33(7)	31(7)	56(7)
C(38B)	221(9)	202(9)	235(10)	10(9)	44(8)	29(7)

Discussion of isotope effects in the generation of isotopologs of 4.

The reaction of **1-*d*$_3$** and **1-*d*$_2$** with $TaCl_2(CH_3)_3$ leads to the formation of **4-*d*$_{2.25}$** and **4-*d*$_{0.84}$**, respectively, with isotopic exchange at the *ipso* position. The exchange is not quantitative in either case indicating that the rates of cyclometallation and protonolysis are not very different. For **1-*d*$_3$** the H incorporation level at the *ipso* position is 75%, while for **1-*d*$_2$** the deuterium incorporation level is 84%. The partial isotope exchange correlates with the ratio of CH_4 to CH_3D generated -- 1.8(1):1 for **1-*d*$_3$** and 1.1(1):1 for **1-*d*$_2$**. The formation of species **C-*d*$_3$** and **C-*d*$_1$** (Schemes 3 and 4) is assumed to occur with quantitative generation of CH_4 and CH_3D, respectively. Hence, from the above ratios of CH_4 to CH_3D, the methane isotopolog ratio corresponding to steps following the formation of **C** can be calculated. For **C-*d*$_3$** (the intermediate in eq (1) of the article, see Scheme 3 below) the ratio of CH_4 to CH_3D (28:72) is essentially the same with the ratio of **4-*d*$_3$** to **4-*d*$_2$** (25:75). In the case of **C-*d*$_1$** (the intermediate in eq (2) of the article, see Scheme 4 below) the ratio of CH_4 to CH_3D (96:4) is slightly different from the ratio of **4-*d*$_1$** to **4-*d*$_0$** (84:16). This difference could be due to some H/D exchange from surface [SiO-H] on the glassware to phenolic deuteron that would cause some CH_4 generation upon formation of **C-*d*$_1$**. Comparison of the isotopolog distribution in the products stemming from steps subsequent to the formation of **C** indicates that cyclometallation is faster than protonolysis of a methyl group in all cases, but it is slowed down when a deuteron is present at the *ipso* position, suggesting that σ bond metathesis has an isotope effect larger than that for protonolysis. The precision of these experiments does not allow us to report the ratio of these (k_H/k_D)'s with any confidence, however.



Scheme 3. Protonolysis vs cyclometallation starting with **1-*d*$_3$**.



Scheme 4. Protonolysis vs cyclometallation starting with **1-*d*$_2$**.

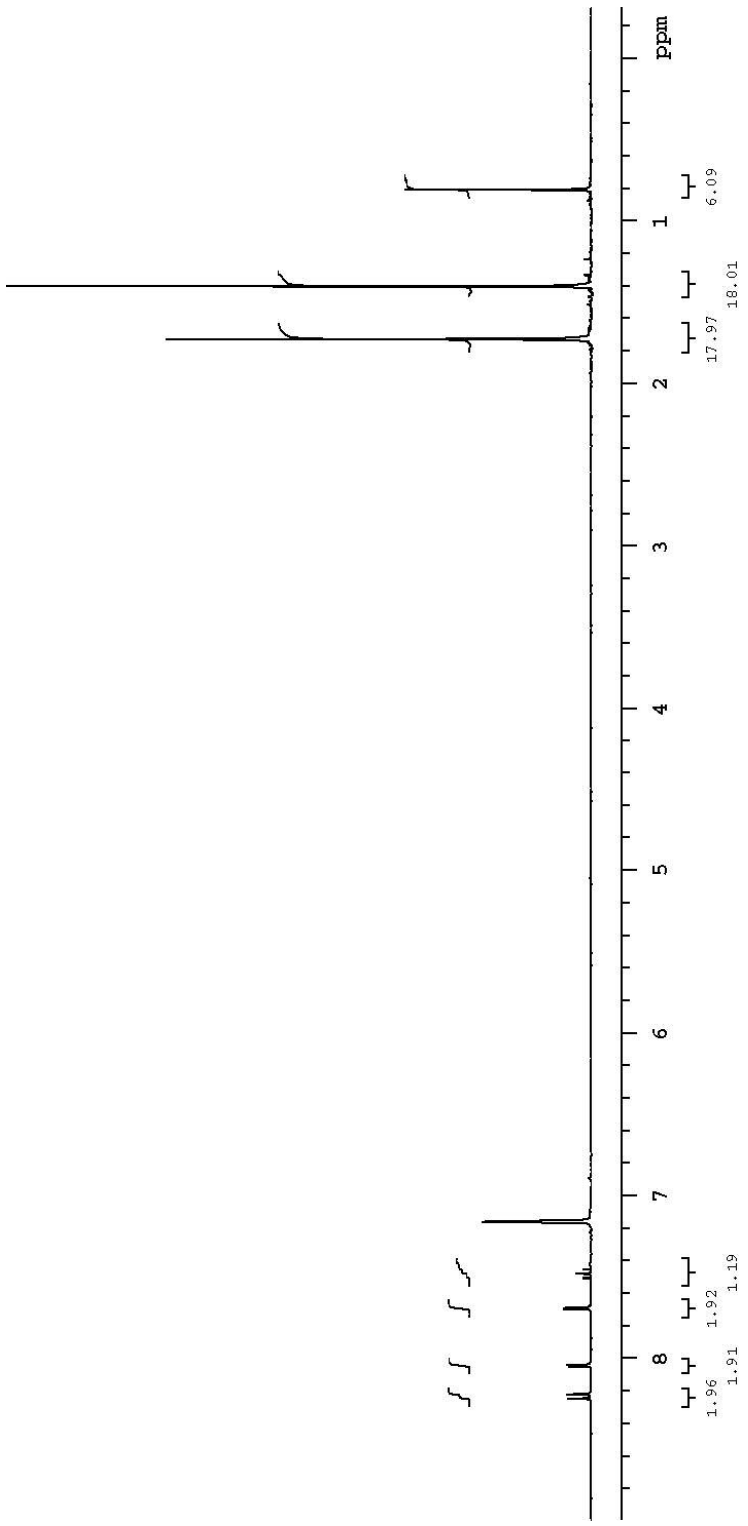


Figure 6. ^{1}H NMR spectrum (C_6D_6) of **3**.

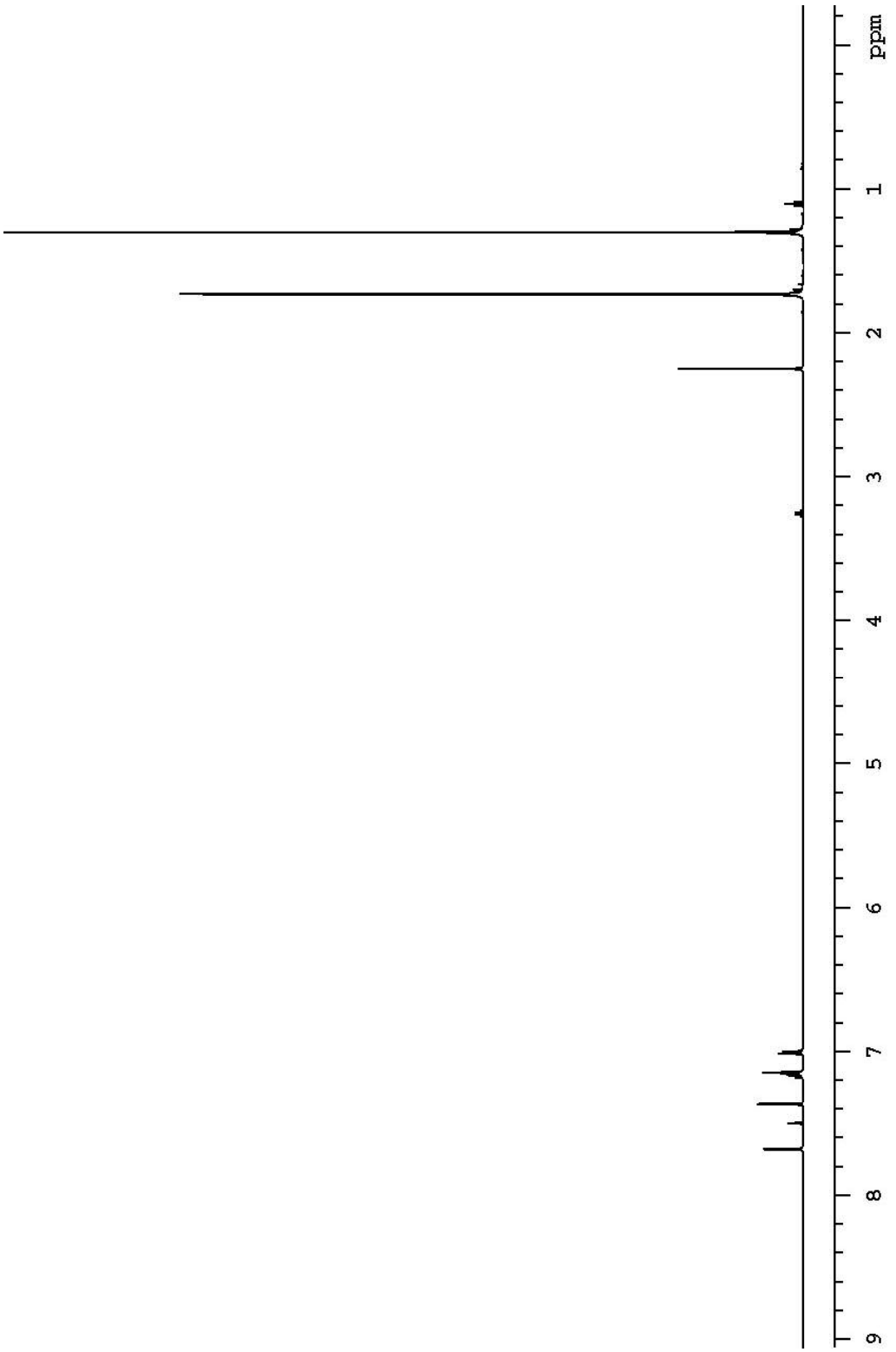


Figure 7. ^{1}H NMR spectrum (C_6D_6) of **4**.

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